

UNCLASSIFIED

AD NUMBER	
AD364082	
CLASSIFICATION CHANGES	
TO:	unclassified
FROM:	confidential
LIMITATION CHANGES	
TO:	Approved for public release, distribution unlimited
FROM:	Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 30 JUN 1965. Other requests shall be referred to Army Missile Command, Redstone Library, Attn: AMSMI-RD-CS, Redstone Arsenal, AL, 35898-5240.
AUTHORITY	
USAMICOM ltr, 1 Feb 1974; USAMICOM ltr, 1 Feb 1974	

THIS PAGE IS UNCLASSIFIED

GENERAL DECLASSIFICATION SCHEDULE

**IN ACCORDANCE WITH
DOD 5200.1-R & EXECUTIVE ORDER 11652**

THIS DOCUMENT IS:

CLASSIFIED BY _____

**Subject to General Declassification Schedule of
Executive Order 11652-Automatically Downgraded at
2 Years Intervals- DECLASSIFIED ON DECEMBER 31, _____.**

BY

**Defense Documentation Center
Defense Supply Agency
Camden Station
Alexandria, Virginia 22304**

SECURITY

MARKING

The classified or limited status of this report applies to each page, unless otherwise marked.

Separate page printouts MUST be marked accordingly.

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C., SECTIONS 793 AND 794. THE TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

Cy 47
CONFIDENTIAL

ROHM & HAAS COMPANY

REDSTONE ARSENAL RESEARCH DIVISION

HUNTSVILLE, ALABAMA

SPECIAL REPORT NO. S-61

APPLICATION OF DTA TO THE THERMAL DECOMPOSITION
OF PROPELLANT AND PROPELLANT INGREDIENTS (U)

364082

CATALOGED BY: DDC
AS AD NO.

PH

U.S. ARMY MISSILE COMMAND

This document contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18, U.S.C., Sections 793 and 794. The transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

DOWNGRADED AT 3 YEAR INTERVALS:
DECLASSIFIED AFTER 12 YEARS.
DOD DIR 5200.10

CONFIDENTIAL

CONFIDENTIAL

ROHM & HAAS COMPANY

REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

REPORT NO. S-61

APPLICATION OF DTA TO THE THERMAL DECOMPOSITION
OF PROPELLANT AND PROPELLANT INGREDIENTS (U)

By

Kenneth G. Scrogam

Approved:



Robert W. Walker, Head
Physical & Polymer
Chemistry Section



Orville H. Loeffler
General Manager

June 30, 1965

DA-01-021 ORD-11909 (Z)

CONFIDENTIAL

C O N F I D E N T I A L

ROHM & HAAS COMPANY

**REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA**

ABSTRACT

The use of differential thermal analysis in the study of propellants and propellant ingredients is discussed in depth. Variables influencing the analyses are cited along with a complete description of the equipment and procedure for analysis. Data reduction techniques and pitfalls are interpreted for the novice.

Analyses have been divided into five major groups:

- (1) solids, (2) liquids, (3) monomers and polymers, (4) mixtures and
- (5) propellants. Exemplary thermograms are presented and discussed for each group.

C O N F I D E N T I A L

CONFIDENTIAL

TABLE OF CONTENTS

	Page
INTRODUCTION	
PART I. GENERAL DISCUSSION OF VARIABLES	1
A. Heating Rate	1
B. Physical Properties of Sample	2
C. Reference Material	3
D. Furnace Atmosphere	3
E. Sample Holders	4
F. Thermocouples	4
PART II. DESCRIPTION OF EQUIPMENT	5
PART III. OUTLINE OF PROCEDURE	10
A. Sample Preparation	10
B. Reference Material Selection and Preparation	10
C. Heating Rate Selection	12
D. Thermocouple Arrangement	12
E. Analysis of Sample	14
PART IV. DATA REDUCTION	14
PART V. EXPERIMENTAL	17
A. Solids (Thermograms No. 1 thru No. 9)	17
B. Liquids (Thermograms No. 10 thru No. 17)	18
C. Monomers and Polymers (Thermograms No. 18 thru 32)	19
D. Mixtures (Thermograms No. 33 thru No. 46)	21
E. Propellants (Thermograms No. 47 thru No. 60)	21
SUMMARY	22

CONFIDENTIAL

CONFIDENTIAL

INTRODUCTION

Recent developments in the field of electronics have led to a widespread interest in the methods of differential thermal analysis (DTA). Thermal analysis may be defined as "The process of determining the temperature at which changes in atomic arrangement accompanied by a usually abrupt change in heat content occur, . . . by observing the aberrations which the heat content changes impose on the rate of temperature change of a specimen situated in an environment whose temperature is changing in a known manner."¹ Differential thermal analysis involves the use of both a test specimen and a reference material as a comparison standard. The latter is, ideally, an inert material possessing the same heat capacity and heat transfer characteristics as that of the sample while at the same time exhibiting no thermal activity throughout the temperature range of the analysis.

In this report discussion will be limited to those aspects of DTA which have been found to be pertinent to the use of the method as a research tool particularly oriented to solid propellants and their components.

¹ Smothers, W. J. and Chaing, Yao, "Differential Thermal Analysis: Theory and Practice", Chem. Pub. Co., Inc., New York, N. Y. 1958, page 37.

CONFIDENTIAL

PART I. GENERAL DISCUSSION OF VARIABLES

In the discussion of any experimental procedure or apparatus it is of the utmost importance to consider the variables in order to ascertain the influence of experimental conditions upon the resultant data. This is even more mandatory in the case of differential thermal analysis. Although the chemical reaction or reactions associated with the change in heat content in the system usually remain unidentified, due to the heterogeneity of the system, reproducible thermograms for a given system are quite readily obtained provided certain experimental conditions are satisfied. The following factors have been found to influence the analysis to varying degrees depending upon the relationship between the variable and the remaining experimental conditions.

A. Heating Rate

The first thing to be said about this variable is that it is absolutely necessary to be able to reproduce the rate of temperature increase within the sample with time in order to obtain reproducible thermograms. Normally this is most easily accomplished with the use of a linear rate of heating, although theoretically, the use of a reproducible non-linear rate should prove to be quite satisfactory. This discussion will be limited to the use, and the effects thereof, of linear rates exclusively. When heating at a linear rate in our system, acceptable control of the furnace temperature has been found to be obtained only when the sensing thermocouple of the control system is situated in the immediate vicinity of the furnace winding. Otherwise, temperature cycling around the control point is observed.

When good heat transfer from furnace to sample holder to sample is exhibited, programming of the furnace temperature will be found to be adequate. However, if an appreciable lag between the temperature

of the furnace and that of the sample is encountered, provisions must be made to control the temperature of the reference material instead of the furnace to provide the linear rate. (This becomes necessary because the lag itself, in all probability, will not be constant over the temperature range of analysis).

The magnitude of the heating rate will influence the analysis almost as much as any one arbitrarily chosen factor. With all other factors held constant, an increase in heating rate will result in an increase in the temperature at which the peak exotherm occurs, if the reaction producing the heat possesses an activation energy. (This statement is valid only if the rates are not extremely high. At very high rates such parameters as thermal conductivity of the sample, change in decomposition mechanism, particle size, etc. may interact to give a limiting experimental value).

B. Physical Properties of Sample

The physical properties of a specimen make a major contribution to the resultant data of a differential thermal analysis. Liquids tend to give better thermograms than solids. This is probably due to two factors: 1) better heat transfer through the sample, and 2) more intimate contact with the sensing thermocouple. On the other hand, liquids may be very difficult to analyze if their viscosity is very high, especially if one desires to analyze very small samples.

For solids the most important consideration in physical properties is the particle size. Finely divided solids give the best results, since poor heat transfer and inadequate thermocouple contact increase with larger particles.

The total weight of the sample is probably the largest single contributing factor in changing the shape of the curves in the

thermogram. Large samples tend to give broad, poorly resolved peaks, and for some high energy propellants or their components, also tend to give explosions which terminate the analysis. On the other hand small samples give sharp, well-defined peaks and are less prone to explode at peak exotherm temperatures. Shifts in the position of the peak exotherm temperature may be observed with changes in sample size, but these shifts are probably more closely associated with bulk density and heat transfer than with the actual weight of the sample. (Shifts will always be observed if the temperature of the reference is being plotted against ΔT and the quantitative heat transfer of the sample and reference are not equal).

C. Reference Material

The choice of a reference material to be used for a particular analysis is sometimes difficult and quite often ends in a compromise. Ideally, it is desirable to have a reference material of the same heat capacity and physical state (solid or liquid) as that of the sample. It is also necessary that the reference material have no thermal activity over the temperature range of analysis.

The most obvious result of a poorly chosen reference material is a continuing baseline shift. Although in specific analyses small amounts of baseline shift may be tolerable, it is very undesirable where measures of small exotherms or endotherms are attempted.

Of all the materials available, Al_2O_3 is probably most often used as a reference material. However, such materials as quartz, MgO , NaCl , isophthalic acid and paraffin oil have been used quite successfully in certain applications.

D. Furnace Atmosphere

It is well known that the atmosphere surrounding the sample does contribute to those reactions where oxidation occurs and/or

gaseous decomposition products are evolved.

E. Sample Holders

One of the first and still widely used sample holders for differential thermal analysis was the furnace block itself. However, in the case of corrosive or very reactive materials or explosives, this becomes very undesirable. The choice of a sample holder then becomes one of compromise between non-reactivity, heat transfer and economy. With respect to the latter, it is desirable to have a sample holder which is disposable, especially in the case of those materials listed above. It is for this reason primarily, that we have chosen quartz tubes to contain the sample and reference materials. Although some unreactive metal, such as nickel, platinum or monel would in some cases be better, the quartz tubes used in this work have been found to be quite adequate.

One other requirement which must be met by the sample holder, in addition to being chemically inert, is that it possess good heat transfer properties. Otherwise, a lag will be developed between the temperature of the furnace and that of the sample resulting in a non-linear heating rate for the sample itself.

F. Thermocouples

In the consideration of all the variables in a differential thermal analysis, that of thermocouples is probably least influential, providing three fundamental requirements are met: 1) the size of the thermocouple wire should be small such that heat transfer by the wire out of the sample is negligible, 2) the metals of the wire should be inert toward the sample, and 3) the size of the thermocouple junction should be as small as possible in order to obtain optimum response.

Difficulties with reproducibility may be encountered if the thermocouples are not geometrically centered in the specimen, but this is more of a problem with technique than one of a variable.

PART II. DESCRIPTION OF EQUIPMENT

The apparatus required for differential thermal analysis may be conveniently divided into three categories: A) a temperature programming and control system, B) a furnace with the control and readout thermocouples and C) an amplifier and readout recorder.

In Category A three pieces of electronic equipment are used to obtain a linear increase in the furnace temperature. They are:

1. Temperature Programmer - Leeds & Northrup
Program Control Unit 10170.
2. Recording Controller - Leeds & Northrup Series
60 Control using 3-Action Current Adjusting
Type (C. A. T.) Control Unit, present range,
0-500°C.
3. Magnetic Amplifier - Fidelity Instrument Corporation,
Fincor Regulator Model, No. MA300A, 300
watts.

As shown in Fig. 1, this equipment is connected in the following manner: A cam with the desired rate of temperature rise is fabricated and affixed to the program control unit. The output of this unit along with the output of the control thermocouple located in the furnace block is fed to the recording controller. A bridge circuit is formed by the program unit slidewire, the recorder control slidewire and the relay unit. As shown in the Figure, the relay unit is connected in the bridge circuit in such a way that any unbalance in the bridge will be detected by the relay input circuit, thereby effecting relay action to position the controlling mechanism.

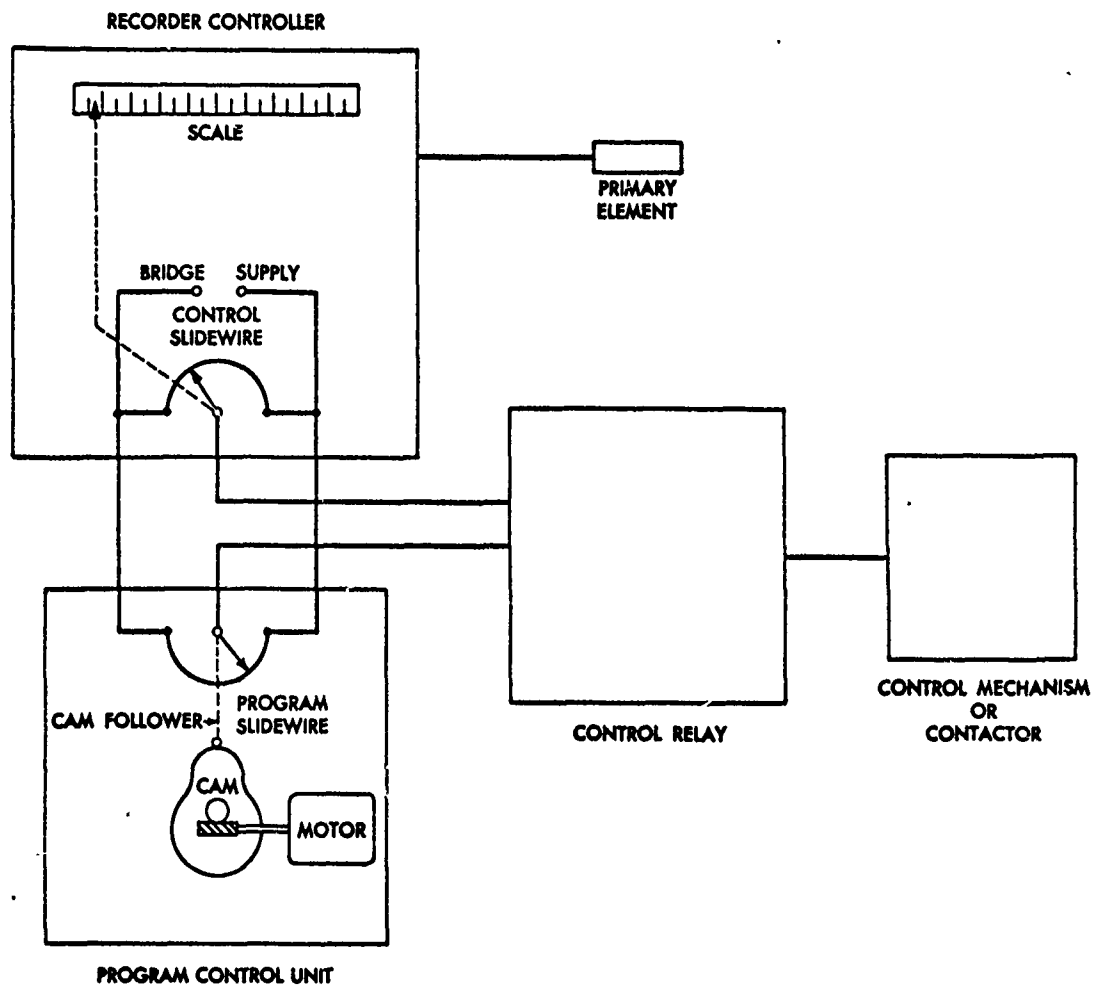


Fig. 1 Block diagram of program control circuit.

Rotation of the cam in the program unit moves its slide-wire contact to create such an unbalance. The relay unit will respond to this unbalance and will effect a change in the controlling mechanism and controlled process. This change will be detected by the measuring element of the recorder, thereby causing the recorder measuring circuit

to reposition the recorder control slidewire. When the control slidewire moves to a position where the bridge is balanced, the controlling action of the relay unit ceases. This control point will be maintained until further rotation of the program unit cam again unbalances the bridge or until the measuring element of the recorder detects a change in the controlled process. Figure 2 shows a typical readout from the recording controller showing the linearity of the heating rate.

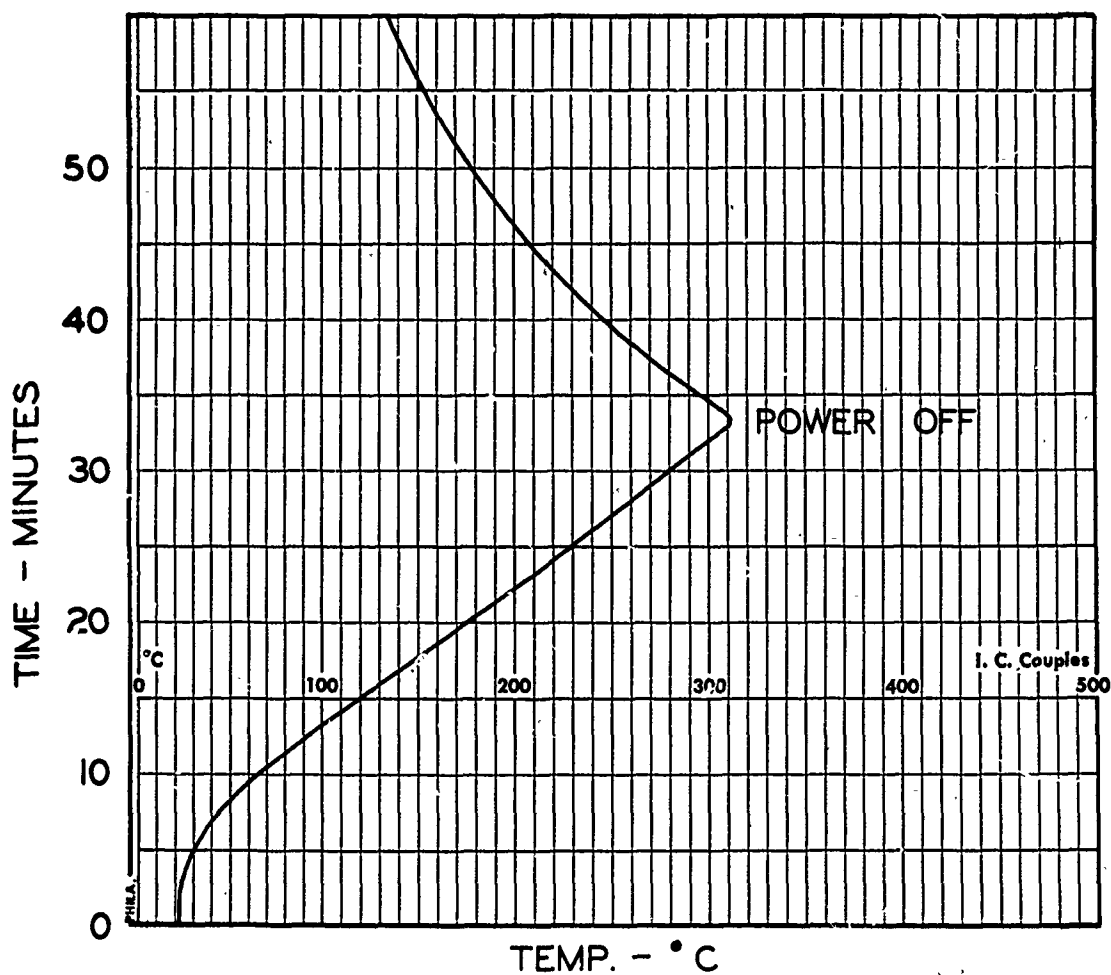


Fig. 2 Heating rate linearity.

The furnace presently in use at this installation is the result of several months of development work. Due to the nature of the materials for which an analysis is required, the furnace should meet a number of qualifications. They are as follows: 1) The construction of the furnace should be simple and economical. 2) The furnace should have rapid response to the command of the temperature programmer. In order to obtain this, it is necessary to have good heat transfer from the electrical windings to the block itself. 3) The furnace should be reasonably durable since some analyses terminate in explosion. 4) A fairly rapid cool-down time is desirable in order to facilitate a reasonable number of analyses per day. 5) Both the electrical and thermal insulation should be adequate to accommodate temperatures up to 500°C. 6) Provision for convenient change of thermocouples, both control and differential, should be available. 7) The apparatus should be capable of analysis in both static and dynamic atmospheres with provisions for gas inlet and outlet. 8) Venting capabilities in the instances where analyses terminate in explosion are also very desirable.

All of the above features have been incorporated into the furnace presently in use. As shown in Figure 3 the furnace is divided into two major parts, a thin-walled cylindrical shell and a removable block which fits into this shell. The electrical windings are insulated from the shell with ceramic beads. Both the shell and block rest on a graphite support which in turn is attached to the aluminum base. Good heat transfer is effected by the snug fit of the block in the heater, along with asbestos insulation on the outside of the heater. Cool-down time of the furnace is minimal since the block is removable thus exposing the inner surface through the use of Amphenol®¹ thermocouple

¹Trademark, Amphenol-Borg Electronics Corporation, 1960.

CONFIDENTIAL

-9-

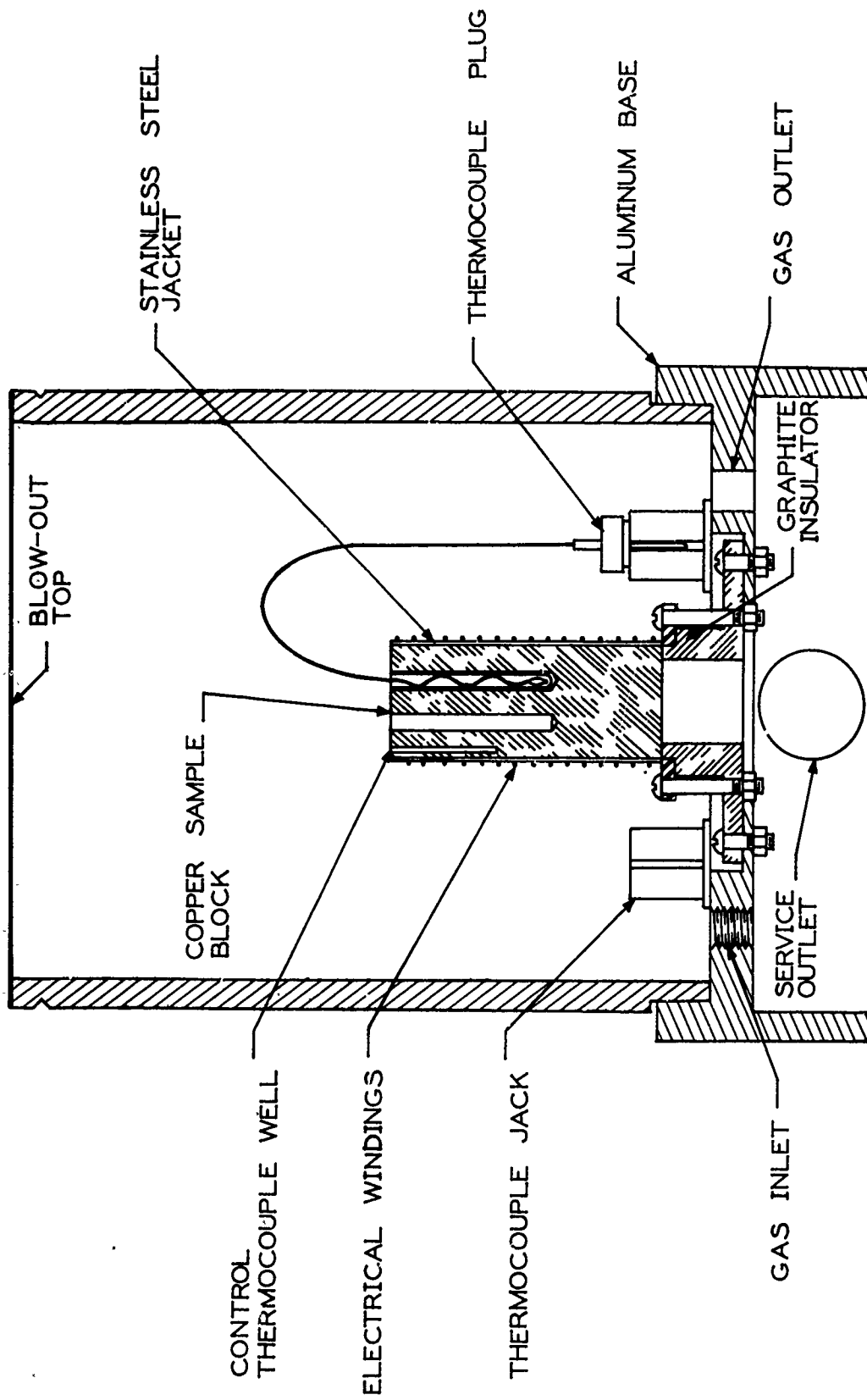


Fig. 3 DTA furnace assembly.

CONFIDENTIAL

connectors. Electrical connections to form the differential thermocouple and to reference the output to 0°C. are made below the base of the furnace.

The furnace may be used with either a static or dynamic atmosphere at atmosphere pressure. The enclosure is fabricated with the top open and thin polyethylene sheet is used to form a blow-out top to exhaust the gasses in the event of an explosion.

PART III. OUTLINE OF PROCEDURE

The procedure used for analysis of a given sample may be conveniently divided into five steps. They are:

A. Sample Preparation

Since samples usually fall into two categories, liquid and solid, the preparation varies depending upon the physical state. Liquids are usually analyzed as received in amount of approximately twenty microliters. This volume is delivered to the sample tube via a microsyringe or elongated dropper. Solids are also analyzed as received if the material is crystalline and the sample is finely divided. If the sample is considered explosive and is not finely divided, it is ground remotely in a mortar with a pestle. Samples of solid propellant are prepared by cutting with a razor blade or other sharp instrument until the particle size is 1 mm.³ or less.

For all solids except propellant, 15-20 milligrams of the material are introduced into the sample tube without packing. For solid propellants it has been found that lightly packing the particles with an applicator stick produces a better defined thermogram.

B. Reference Material Selection and Preparation

As discussed in Part I, the choice of a reference material for a particular analysis is sometimes difficult. In the case of solids, a

CONFIDENTIAL

-11-

reference material chosen because the particle size and heat transfer characteristics approximate those of the sample may have a heat capacity sufficiently different to eliminate its use. On the other hand, when heat capacities are matched, problems may be encountered because of heat transfer properties. The solution to all of these problems is quite often a compromise in the selection of a reference material.

Seven different reference materials have been used in conjunction with the analysis of solid propellants or their components. Of the four liquids that have been used, dibutyl phthalate (DBP) is probably the one used most often. This compound has no detectable thermal activity from room temperature to its boiling point ($340^{\circ}\text{C}.$) and its heat capacity very closely approximates that of many of the liquids which we have analyzed. Nujol, or mineral oil, Kel-F oil (No. 1 and No. 10) and benzyl butyl phthalate (BBP) are other liquids which we have used for reference materials.

With respect to solids, aluminum oxide is the universal favorite. A well documented reference material, this compound has been used for virtually all our solid analyses, most mixtures and even some liquid analyses. For analyses where the heat capacity of aluminum oxide is too high, isophthalic acid (IPA) has been used. However, this compound is useful only to its melting point ($345^{\circ}\text{C}.$).

Solid propellants present yet another problem in the selection of a reference material. Here, in most instances, we have a mixture of a polymer, a liquid and two or more solids jelled into a rubbery mass. No single compound or substance is likely to equal this heterogeneity, but Al_2O_3 or IPA have been found to be adequate. A dummy solid propellant composed of inert ingredients is presently undergoing tests to be used as a reference material in place of these two compounds.

CONFIDENTIAL

C. Heating Rate Selection

A heating rate of 10°C./min. is usually chosen for both solid propellants and their ingredients. The selection is purely arbitrary and is chosen for two reasons. First, this rate allows up to ten analyses during the work day, whereas a very slow rate would permit only one or two, and second, the rate is sufficiently fast to avoid the major pitfall of a very slow rate, i. e., the loss of sensitivity due to small heat losses over long periods of time.

The heating rate should be kept constant if legitimate comparison of the thermal properties of different materials is to be made, unless data on each compound at various heating rates is available.

D. Thermocouple Arrangement

The thermocouples used in a differential thermal analysis form the backbone of the experiment. Consideration must be given to both the electronic and physical arrangement in the design of the experiment. As shown in Fig. 4 the electronic arrangement in use with our system is very simple and straightforward. The output of a differential thermocouple is fed through a DC amplifier to the "Y" axis of an X-Y recorder while the output of the thermocouple in the reference material is referenced to 0°C. and fed to the "X" axis.

The physical arrangement of the thermocouples is somewhat more complicated. This arises from the fact that it is necessary to have the thermocouple bead in the geometrical center of the specimen in order to obtain reproducible results. For our system, this is accomplished in one of two ways. The first is to use 2-hole ceramic tubing (3 mm. o. d.) which fits snugly into the sample tube. This automatically centers the thermocouple in the horizontal plane. Centering in the vertical plane is then accomplished with a ribbon of tape placed on the ceramic at the top of the sample tube. This method is very ade-

quate except in the instances where appreciable amounts of gas are evolved during the analysis. When this is the case, it is better to use the second method of centering and support. This method consists of removing the outer insulation from a set of thermocouple wires (B & S. gauge No. 28) and twisting the insulated iron and constantan wires together. After the thermocouple bead is made, the wires adjacent to the bead are separated to a distance equal to the inside diameter of the sample tube, thus centering the bead in the horizontal plane. The remaining twisted wires are then formed in a see-saw fashion to allow positioning in the vertical plane. This method allows evolution of gas with virtually no obstruction.

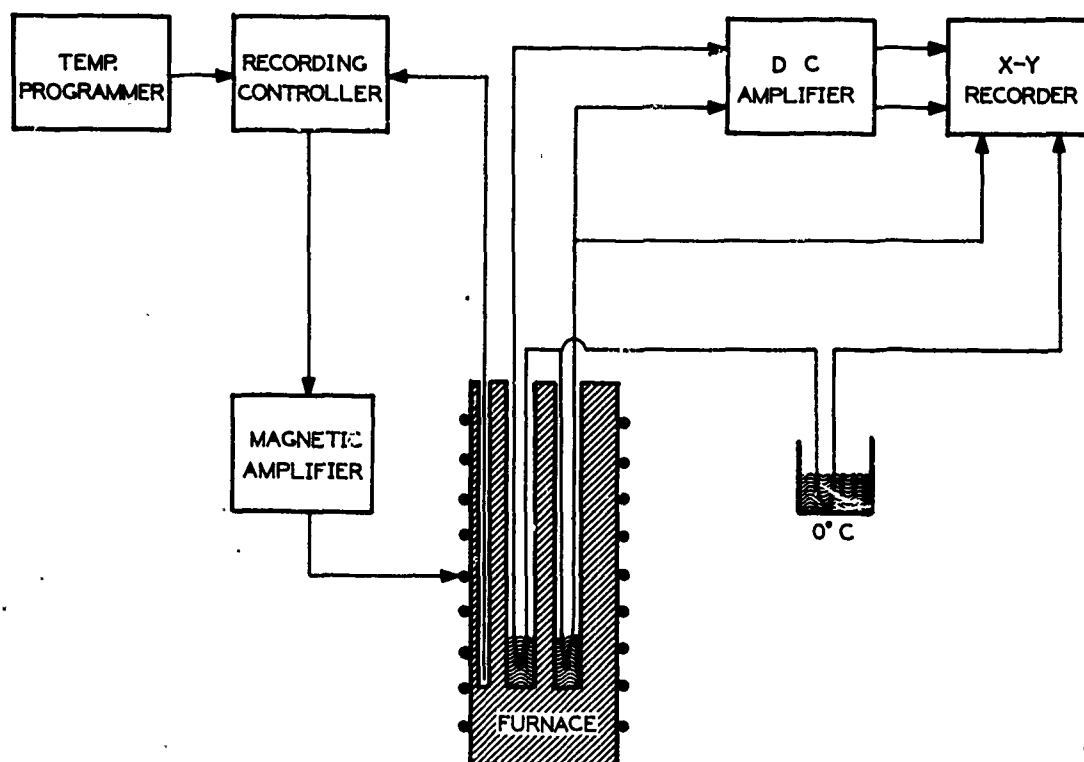


Fig. 4 Diagram of DTA apparatus.

E. Analysis of Sample

All electrical connections are made to the instrumentation and the temperature program started. The analysis is terminated when the decomposition is obviously completed and ΔT has returned to zero. It should be noted that in many instances, the baseline will be shifted after the decomposition is completed. This is perfectly normal and should be expected in all instances where there is a loss of material during the decomposition.

PART IV. DATA REDUCTION

Two factors share equal degrees of importance in data reduction. The first relates to the peak temperature. If the temperature of the reference material (T_r) is monitored as a function of the differential temperature (ΔT), the thermogram will appear as shown by the solid line in Figure 5. If the temperature of the sample (T_s) is plotted on the X-axis of the readout, the thermogram will appear as shown by the dotted line. If the temperature of the block (T_b) is used for the X-axis the peak shape will approximate that of T_r and the position of the peak on the temperature scale will be equal to or lower than that for T_r . The amount of downfield shift in T_b compared to T_r will depend on the temperature lag of the block behind the reference material at the temperature of peak deflection. The amount of upfield shift in T_s compared to T_r will depend upon several factors. Among these are the weight of the sample, the heating rate, the rate of the reaction, the temperature at which the reaction occurs and other factors contributing to the heat loss characteristics of the particular sample undergoing analysis.

With these facts in mind it is easy to see why T_r is chosen for the X-axis in most DTA work. The temperature of the reference material at maximum deflection is by far the most reproducible of the three under consideration. Although the absolute temperature of the

CONFIDENTIAL

-15-

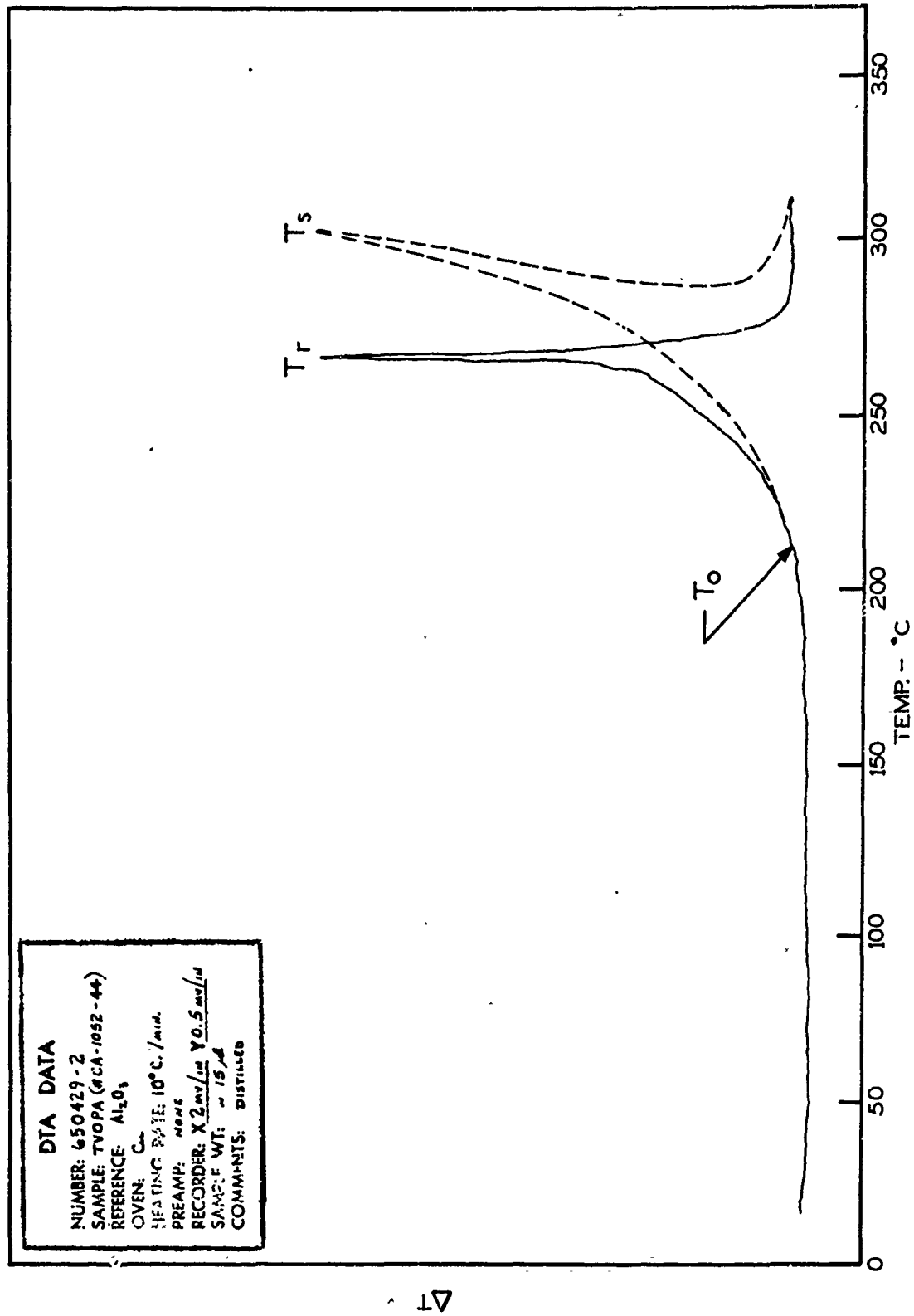


Fig. 5 Comparison of T_r and T_s .

CONFIDENTIAL

sample may be higher or lower at maximum deflection, the relative time at which the reaction occurs in the temperature regime will very nearly be the same. If it is desired to know the actual sample temperature at peak deflection, this is readily obtained by adding ΔT to the reference temperature, T_r , i. e.,

$$T_s = T_r + \Delta T.$$

The second factor of importance in data reduction is related to the interest in the temperature at which exothermic decomposition is first detected, or T_o as it is labeled in Figure 5. Obviously, this depends to a great extent upon the sensitivity of the instrumentation; the more ΔT is amplified, the lower the temperature a deflection from the baseline may be observed. However, as the amplification is increased the linearity of the baseline is decreased thus making it difficult in some instances to tell the difference between what is the baseline and what is a deflection from the baseline.

The temperature of onset of exotherm is also influenced by the characteristics of the furnace which stem primarily from minor differences in symmetry incorporated during the construction. A small misalignment of one of the wells in the block or a small difference in the depth of the two wells is sufficient to modify the heat transfer characteristics enough to cause trouble in the baseline with a highly-amplified ΔT .

Considering all of these factors wide variations in T_o of the same sample analyzed on different instruments could easily be expected. However, carefully controlled experimental conditions, using the same apparatus, will give reproducible values of T_o which may, in turn, be compared with those of different materials.

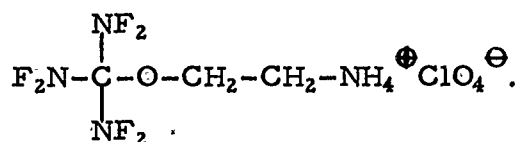
PART V. EXPERIMENTAL

Differential thermal analysis has been used to establish the thermal characteristics of several solid propellants and their components. Although a majority of the work is in the field of N-F compounds and N-F propellants, other materials of current interest have been analyzed and a limited number of thermograms of this nature are also presented. All thermograms cited in the following discussion are shown in Appendix A.

The work may be conveniently divided into five major areas: (1) solids, (2) liquids, (3) monomers and polymers, (4) mixtures and (5) solid propellants.

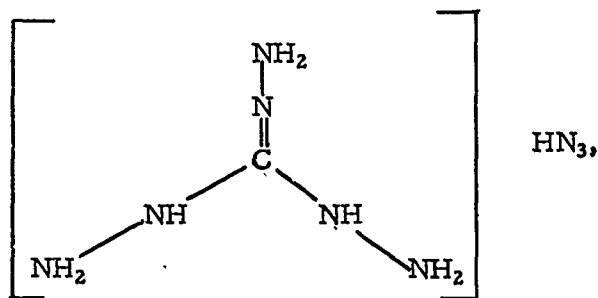
A. Solids (Thermograms No. 1 thru No. 9)

Two of the compounds most often used to check the sensitivity and calibration of a differential thermal analysis apparatus are copper (II) sulfate pentahydrate and ammonium nitrate. Thermograms No. 1 and No. 2 show these two compounds as run on our apparatus. No. 3 shows benzoic acid, a standard calibration compound. Magnesium stearate, boric acid and Cab-o-sil[®]¹, three compounds of current interest as stabilizers are shown in Nos. 4, 5 and 6. The next compound in the group is the conventional solid propellant oxidizer, ammonium perchlorate. Following AP is an NF oxidizer, INFO-635P,



This compound, like AP, has an endothermic phase transition prior to decomposition. Triaminoguanidinium azide or TAZ,

¹ Trademark, Cabot Corporation, Boston, Massachusetts.

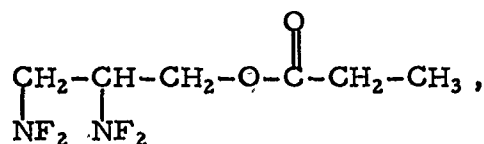


is shown in the last thermogram (No. 9) of the solids group. It is found to decompose exothermically at the boiling point ($\sim 180^\circ\text{C}$.).

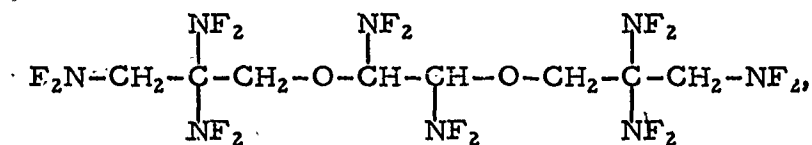
B. Liquids (Thermograms No. 10 thru No. 17)

The thermal activity of 1,2,3-tris[α,β -bis(difluoramino)ethoxy] propane, or TVOPA, is shown in thermogram No. 10. This compound, in our "standard" sample size, is found to undergo decomposition starting at some temperature above 150°C . with the peak temperature occurring around 265°C .

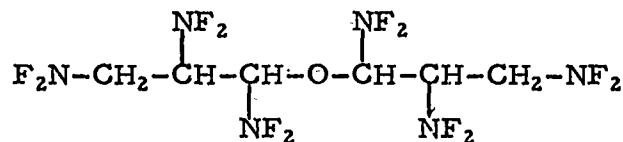
The N_2F_4 adduct of allyl propionate or APA,



is shown in No. 11. This compound has no detectable activity before its boiling point ($\sim 185^\circ\text{C}$.) No. 12 shows OPE,



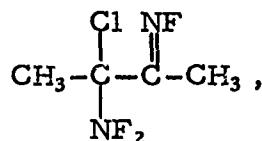
to decompose with a peak temperature of 240°C . Unlike OPE, HPE



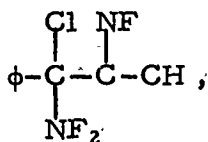
has only minor thermal activity before decomposition at the boiling point.

1,2,4,5,8,9-Hexakis(difluoramino)nonane, HDN, was run and is shown in No. 14. Although this sample was chromatographed, the thermogram shown may not represent the activity of 100% pure material. Other compounds of this nature have not shown the twin-peak activity exhibited here. 1,2,5,6-tetrakis(difluoramino)hexane is found to undergo no visible decomposition before vaporization. This is shown in No. 15.

Two compounds containing the fluorimino group are shown in Nos. 16 and 17. MNFP,



undergoes no activity to the boiling point. Replacement of a methyl group with a phenyl changes the thermal behavior. PNFP,

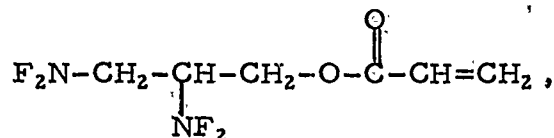


shows an exothermic decomposition around 230°C.

C. Monomers and Polymers (Thermograms No. 18 thru 32).

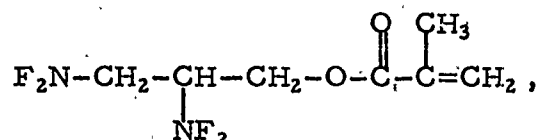
It is within the scope of differential thermal analysis to detect the temperature range of energy release during the polymerization of a monomer. This is shown in thermograms No. 19 and 20 for two monomers, methyl methacrylate and styrene. Both contained AIBN as the initiator. The MMA was run in a solution with dibutyl phthalate. The styrene was polymerized in bulk.

NFPA,



is shown in No. 21. Without initiator, the polymerization is almost always followed immediately by decomposition. With initiator, the polymerization may be effected at a lower temperature and the resultant polymer is found to decompose at 225°C.

NFPMA,



is shown in No. 22. This monomer is found to have parallel behavior to NFPA in its thermal activity.

TAMA or 3[1,2,4,5-tetrakis(difluoramino)]amyl methacrylate is shown in No. 23. Unlike NFPA and NFPMA, this monomer does not exhibit an appreciable polymerization exotherm, and the decomposition temperature is a few degrees lower than that for NFPA or NFPMA.

Thermograms No. 24, 25 and 26 are from analyses on polymers. No. 24 was made on NFPA that had been bulk polymerized, No. 25 was made on NFPA prepolymer and No. 26 on NFPMA polymer. The data show the activity to be the same, regardless of the method of preparation.

The activity of several copolymers has been obtained. A copolymer of NFPA and HPMA, hydroxypropyl methacrylate, is shown in No. 27. NFPMA, HPMA copolymer is given in No. 28. Itaconic anhydride (IA), glycidyl acrylate (GA) and glycidyl methacrylate (GMA) have been used to make copolymers with NFPA and these are shown in

Nos. 29, 30, and 31.

One terpolymer has been analyzed, the components were NFPA, n-butyl acrylate and maleic anhydride. This thermogram is No. 32.

D. Mixtures (Thermograms No. 33 thru No. 46)

Much of the utility of differential thermal analysis in propellant research is manifest in the ability to assess quickly the thermal properties of physical mixtures with very small amounts of materials. This feature has been used on many mixtures of unknown or uncertain thermal properties. Thermograms No. 33 thru No. 39 show the results on TVOPA with such compounds as APA, tetraethyl orthosilicate (TEOS), a urethane, hexamethylene diisocyanate (HMDI), boric acid, tri-n-butyl borate (TBB) and NFPA. NFPA polymer is shown with Cab-o-sil[®] and with HPMA (No. 40 and 41). Poly NFPA with HPMA is also given (No. 42) for comparison purposes.

Three component mixtures have also been run. The next three thermograms (No. 43 thru No. 45) are given as examples.

The method may also be used for determining the activity of a fairly reactive compound (TAZ) with a fairly non-reactive compound (PBAA) as shown in the last thermogram (No. 46) of the series.

Analysis of these data on mixtures readily shows the utility of the method and points out the sometimes radical changes in thermal activity which may be produced by mixing two or more compounds.

E. Propellants (Thermograms No. 47 thru No. 60)

The last group of thermograms presented is that of propellants. The composition of each is given in Appendix B.

CONFIDENTIAL

-22-

The reader will note that in many instances the thermograms have two or more peaks. It should be pointed out that one of these peaks, in most instances, is the superimposition of the endotherm of ammonium perchlorate upon the exotherm of decomposition and thus should not be considered a true peak. This is shown clearly in thermogram No. 51 where the KCl has been substituted for AP in the SA-103 composition. Here we find a single peak for the decomposition of the binder phase.

SUMMARY

Differential thermal analysis is a very useful method in propellant research. It has been demonstrated that the method may be used in most situations. The thermal characteristics of many solids, liquids, monomers, polymers, mixtures and propellants have been established. Using this method along with proper data analysis, significant and valid conclusions may be drawn regarding the sensitivity to heat and the consequences of heating solid propellants and their components.

CONFIDENTIAL

CONFIDENTIAL

APPENDIX A

INDEX TO THERMOGRAMS

<u>No.</u>	<u>Solids</u>
1	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
2	NH_4NO_3
3	Benzoic Acid
4	Magnesium Stearate
5	Boric Acid
6	Cab-o-Sil
7	AP
8	INFO-635
9	TAZ
	<u>Liquids</u>
10	TVOPA
11	APA
12	OPE
13	HPE
14	HDN
15	TNFH
16	MNEP
17	PNFP
	<u>Monomers & Polymers</u>
18	m-MMA
19	m-STY
20	m-p-NFPA
22	m-NFPMA
23	m-TAMA

CONFIDENTIAL

CONFIDENTIAL

APPENDIX A (continued)

24	p-NFPA
25	pp-NFPA
26	p-NFPMA
27	cp-NFPA, HPMA
28	cp-NFPMA, HPMA
29	cp-NFPA, IA
30	cp-NFPA, GA
31	cp-NFPA, GMA
32	tp-NFPA, BA, MALA

Mixtures

33	TVOPA/APA
34	TVOPA/TEOS
35	TVOPA/Urethane
36	TVOPA/HMDI
37	TVOPA/Boric Acid
38	TVOPA/TBB
39	m-NFPA/TVOPA
40	pp-NFPA/Cab-o-Sil
41	p-NFPA/p-HPMA
42	p-NFPMA/p-HPMA
43	m-NFPA/TVOPA/TEOS
44	m-NFPA/TVOPA/Glass Wool
45	m-NFPA/TVOPA/H ₂ O
46	PBAA/TAZ

CONFIDENTIAL

CONFIDENTIAL

APPENDIX A (continued)

Propellants

47	RH-C-2
48	RH-C-14
49	PBAA
50	RH-P-112
51	KGS-1
52	RH-SA-100
53	RH-SA-103
54	RH-SB-103
55	RH-SA-148
56	RH-SA-151
57	RH-SA-156
58	RH-SA-164
59	RH-SB-174
60	RH-SA-203

CONFIDENTIAL

CONFIDENTIAL

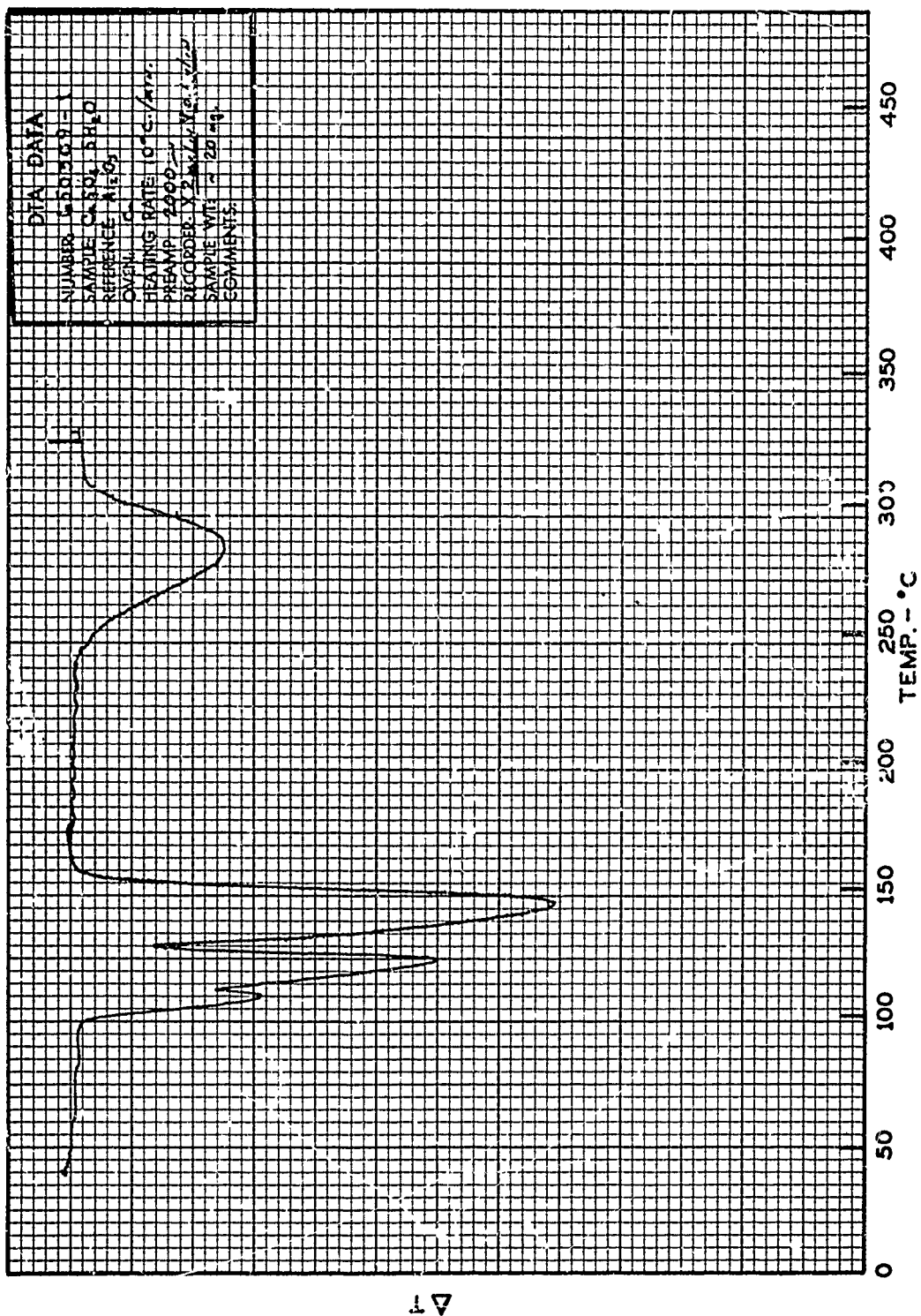
GLOSSARY OF ABBREVIATIONS AND CODE NAMES

AP	-	Ammonium perchlorate
APA	-	2,3-Bis(difluoramino)propyl propionate
BA	-	n-Butyl acrylate
GA	-	Glycidyl acrylate
GMA	-	Glycidyl methacrylate
HDN	-	1,2,4,5,8,9-Hexakis(difluoramino)nonane
HMDI	-	Hexamethylene diisocyanate
HPMA	-	Hydroxy propyl methacrylate
IA	-	Itaconic anhydride
INFO	-	Tris(difluoramino methoxy) ethanolamine perchlorate
MALA	-	Maleic anhydride
MMA	-	Methyl methacrylate
MNFP	-	2-Chloro-2-difluoramino-3-fluorimino butane
NFPA	-	2,3-Bis(difluoramino)propyl acrylate
NFPMA	-	2,3-Bis(difluoramino)propyl methacrylate
OPE	-	1,2-Bis[2,2,3-tris(difluoramino)propoxy]-1,2-bis(difluoramino)ethane
PBAA	-	Polybutadiene, acrylic acid copolymer
PNFP	-	1-Chloro-1-difluoramino-1-phenyl-2-fluorimino propane
STY	-	Styrene
TAMA	-	1,2,5,6-Tetrakis(difluoramino)amyl methacrylate
TAZ	-	Triaminoguanidium azide
TEOS	-	Tetraethyl orthosilicate
TNFH	-	1,2,5,6-Tetrakis(difluoramino)hexane
TVOPA	-	1,2,3-Tris[α , β -bis(difluoramino)ethoxy] propane

CONFIDENTIAL

THERMOGRAM NO. 1

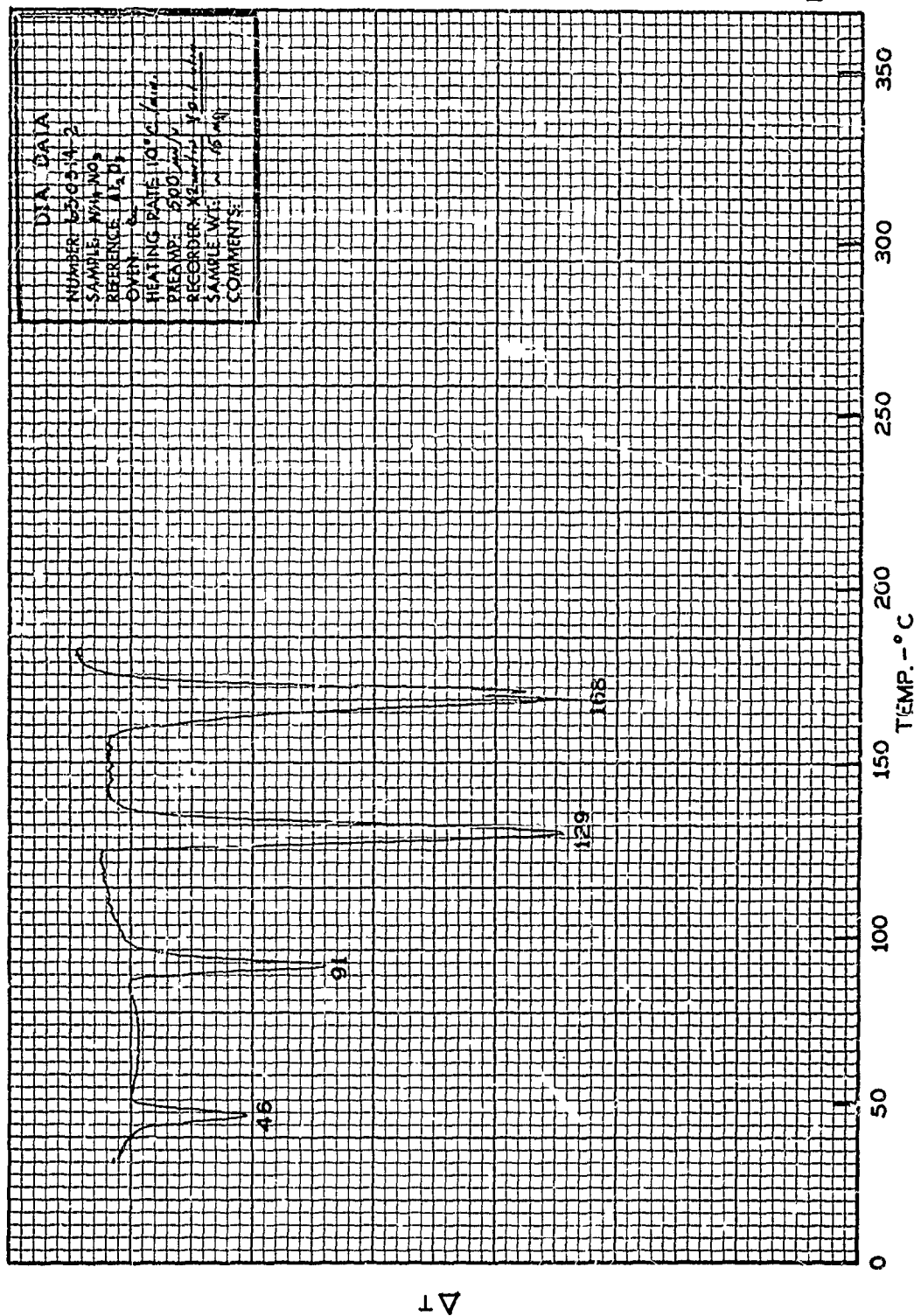
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$



DTA DATA

NUMBER 15013091-1
 SAMPLE $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 REFERENCE Ni_2O_3
 OVEN 15
 HEATING RATE $10^\circ\text{C}/\text{min}$
 PREAMP 1000
 RECORDER X-2200
 SAMPLE WT 0.2014g
 COMMENTS

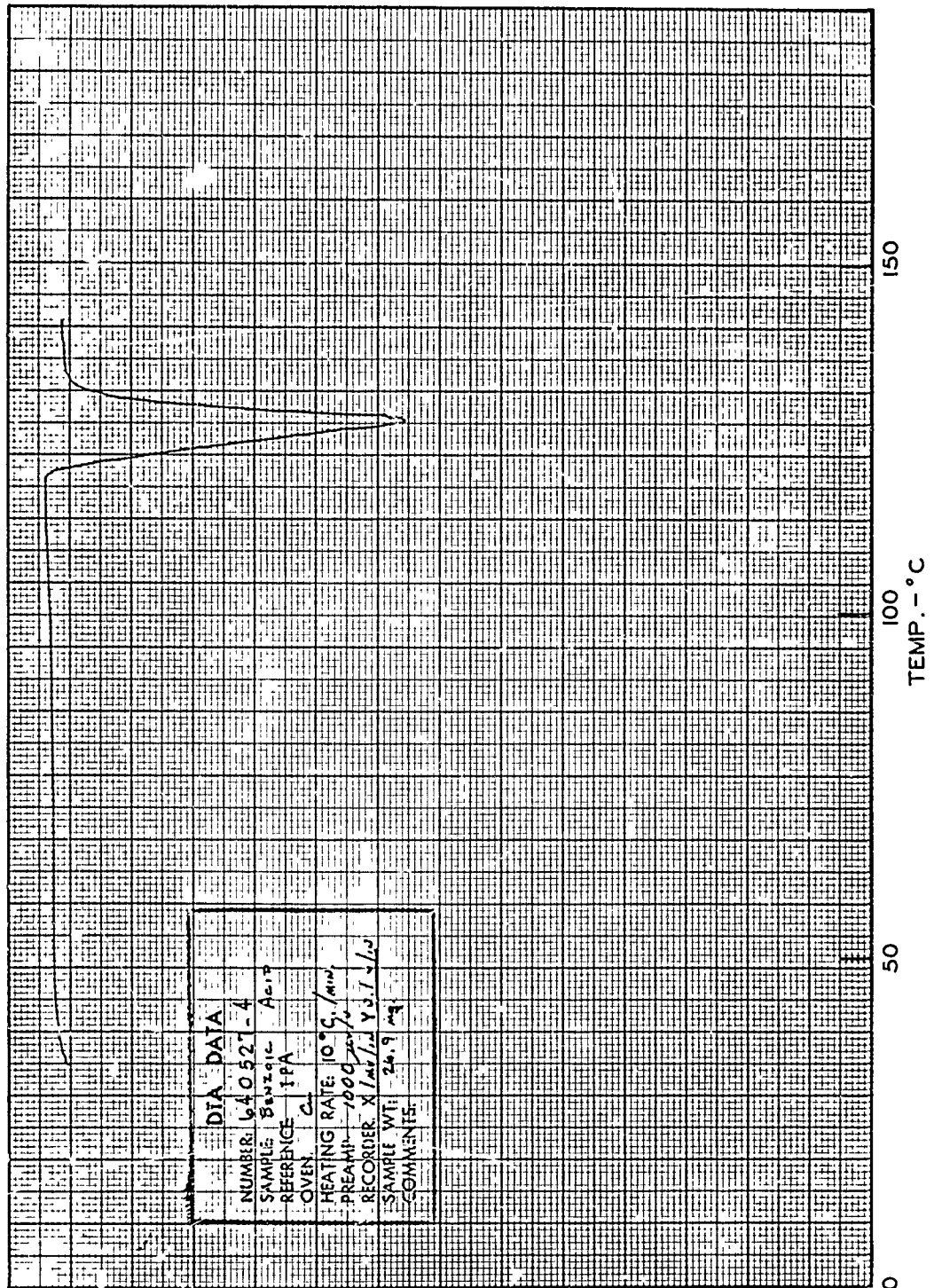
NH_4NO_3



THERMOGRAM NO. 2

BENZOIC ACID

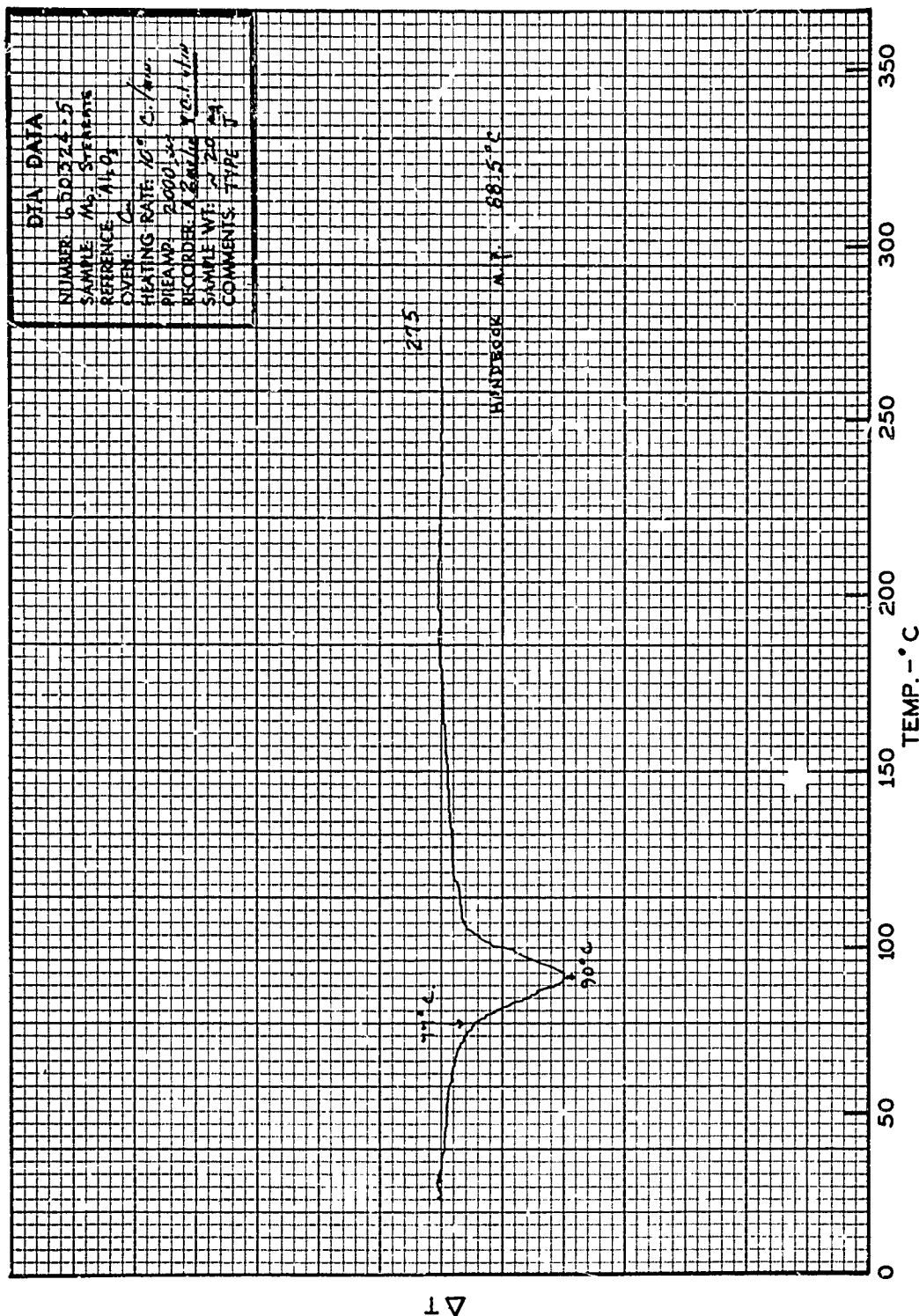
THERMOGRAM NO. 3



DIA DATA	
NUMBER	64 0527-4
SAMPLE	Benzoic Acid
REFERENCE	IPA
OVEN	C
HEATING RATE	10°C/min
PREAMP	1000
RECORD	X 1 mV/in
DATE	Y3.1.10
SAMPLE WT	20.9 mg
COMMENTS	

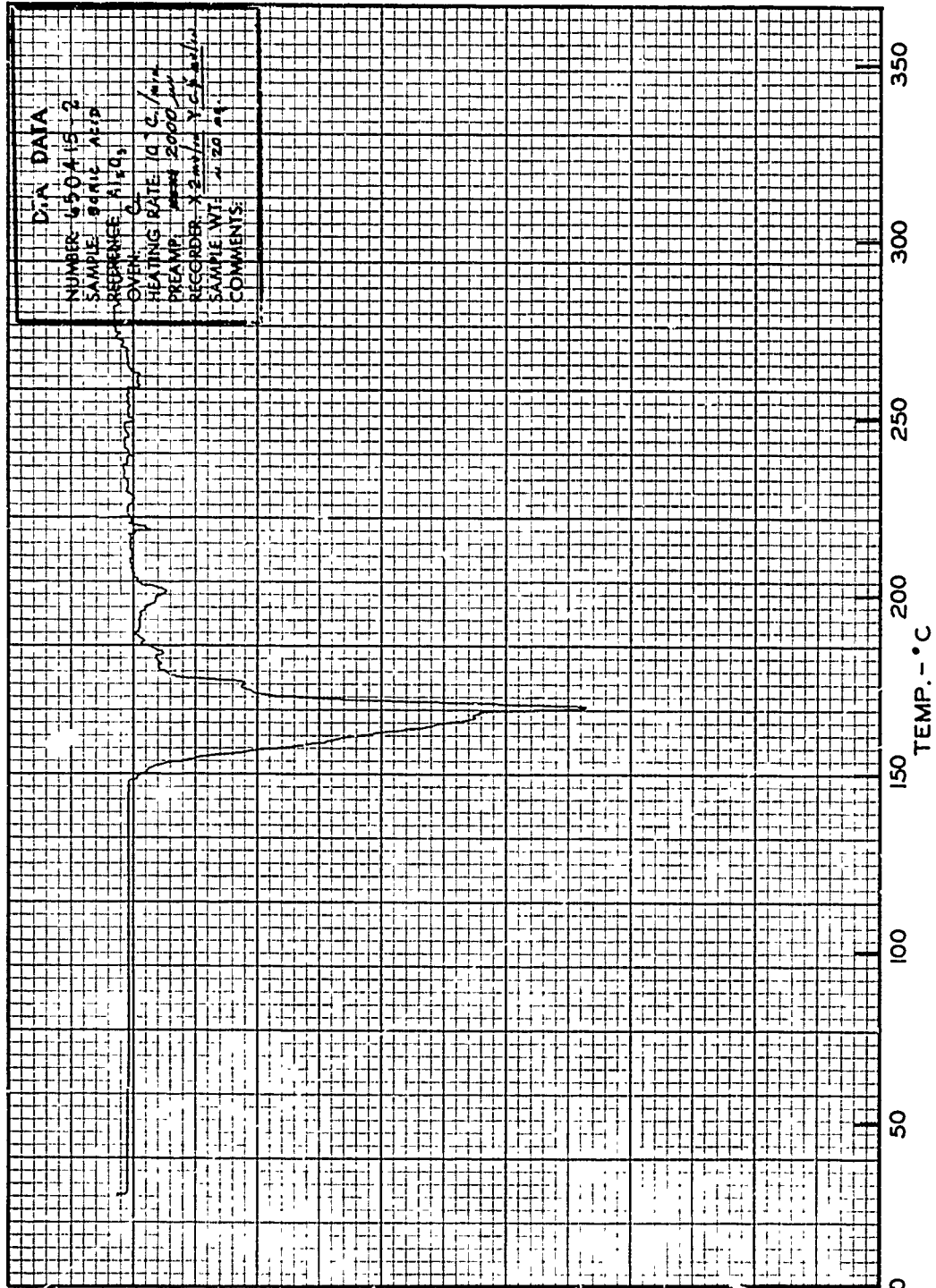
M_G STEARATE

THERMOGRAM NO. 4



THERMOGRAM NO. 5

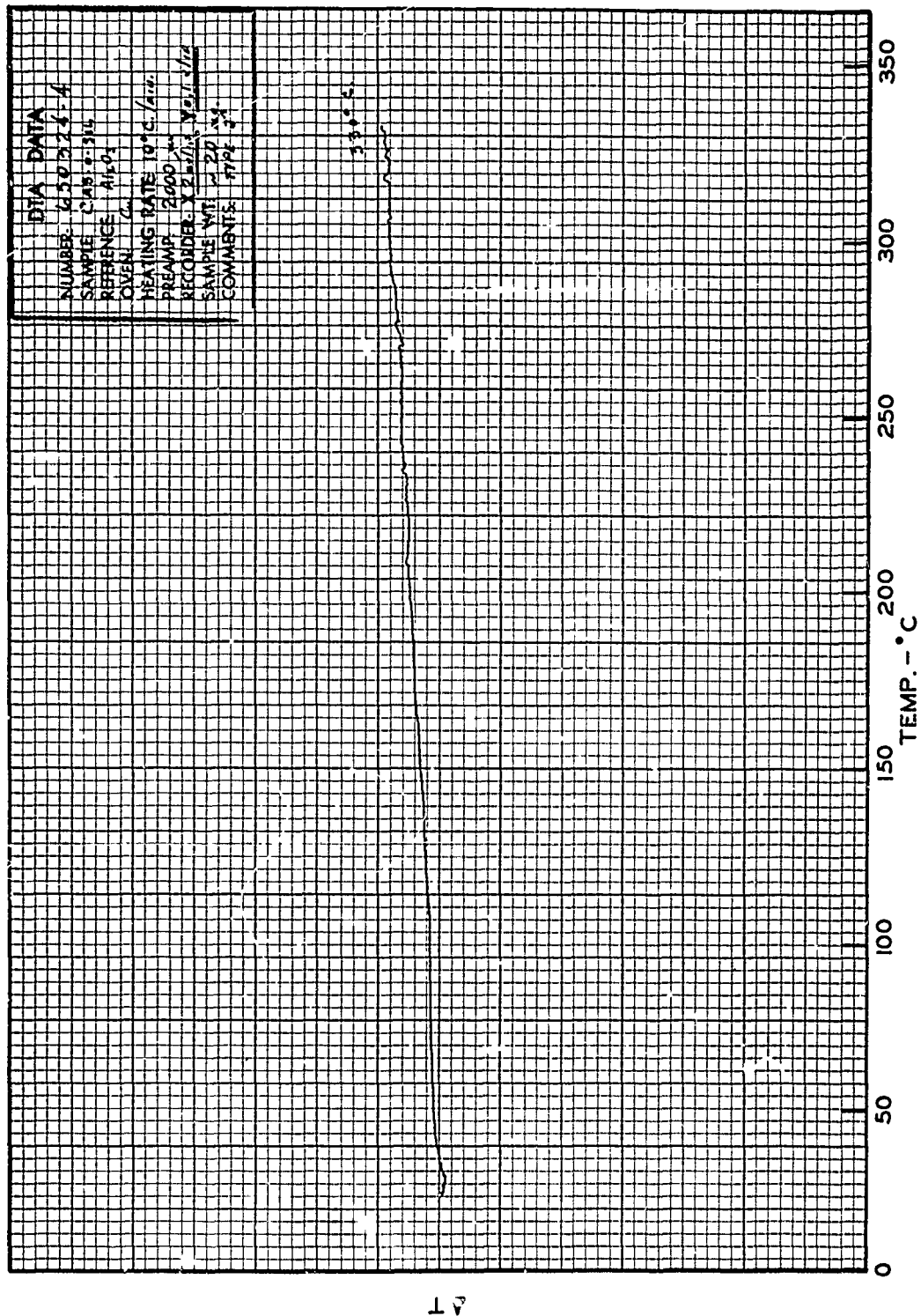
BORIC ACID



1 Δ

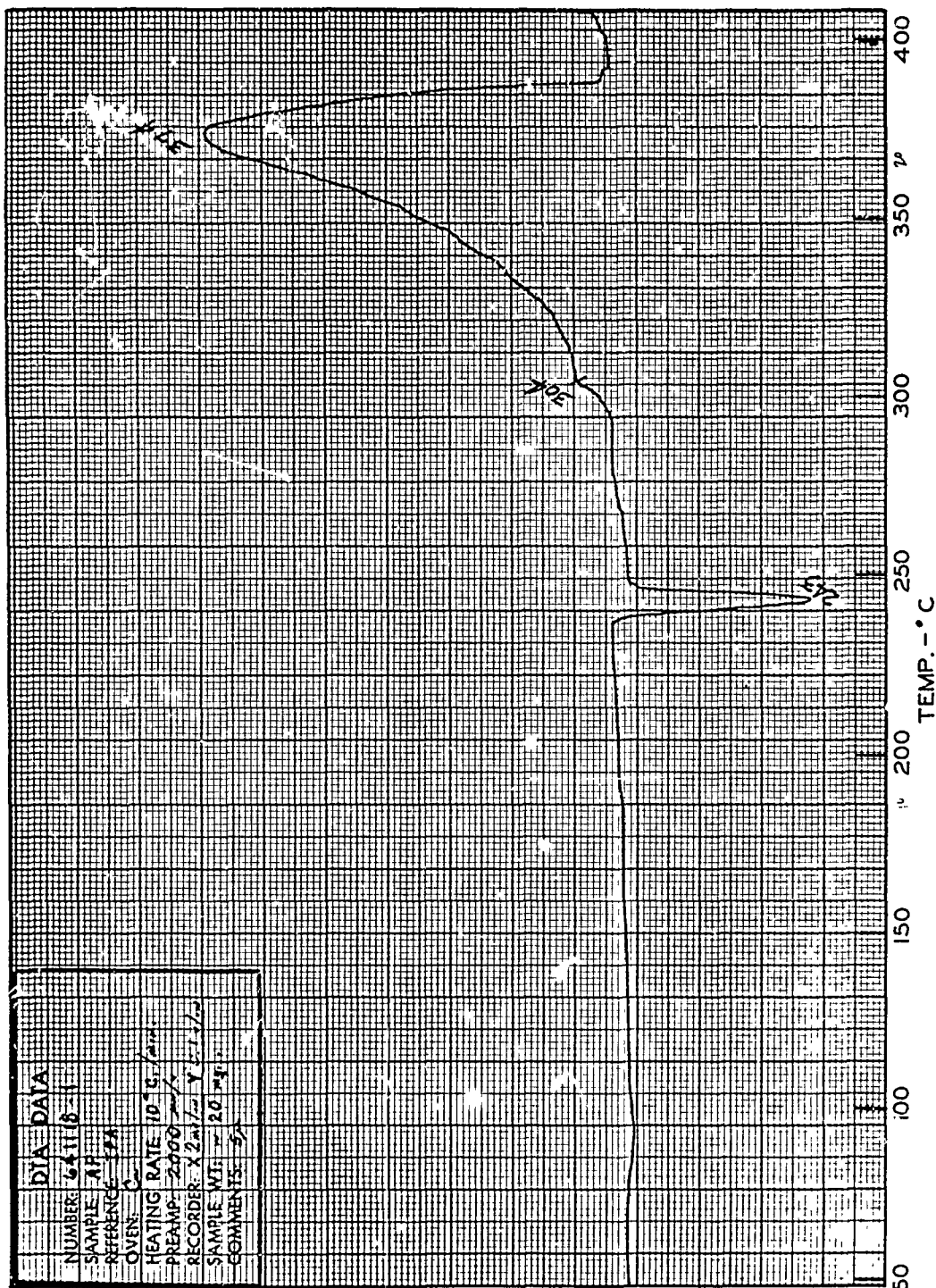
CAB - O - SIL

THERMOGRAM NO. 6



THERMOGRAM NO. 7

AP

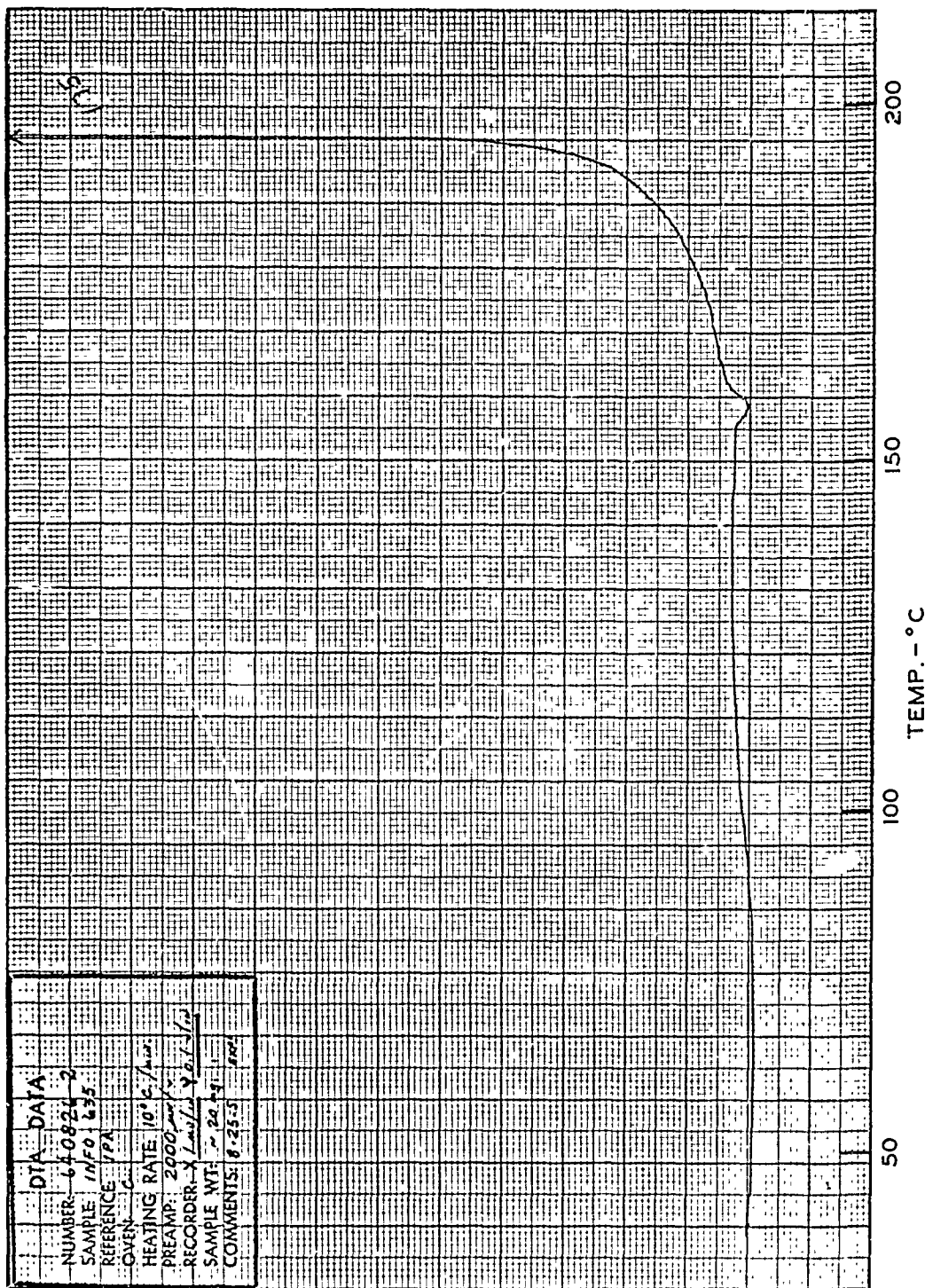


DIA DATA	
NUMBER	64116-1
SAMPLE	AP
REFERENCE	PPA
OVEN	0
HEATING RATE	10°C/min
PREAMP	2000
RECORD	X 2m/sec Y 1.1/20
SAMPLE WT	20 mg
COMMENTS	52

ΔT

INFO - 635P

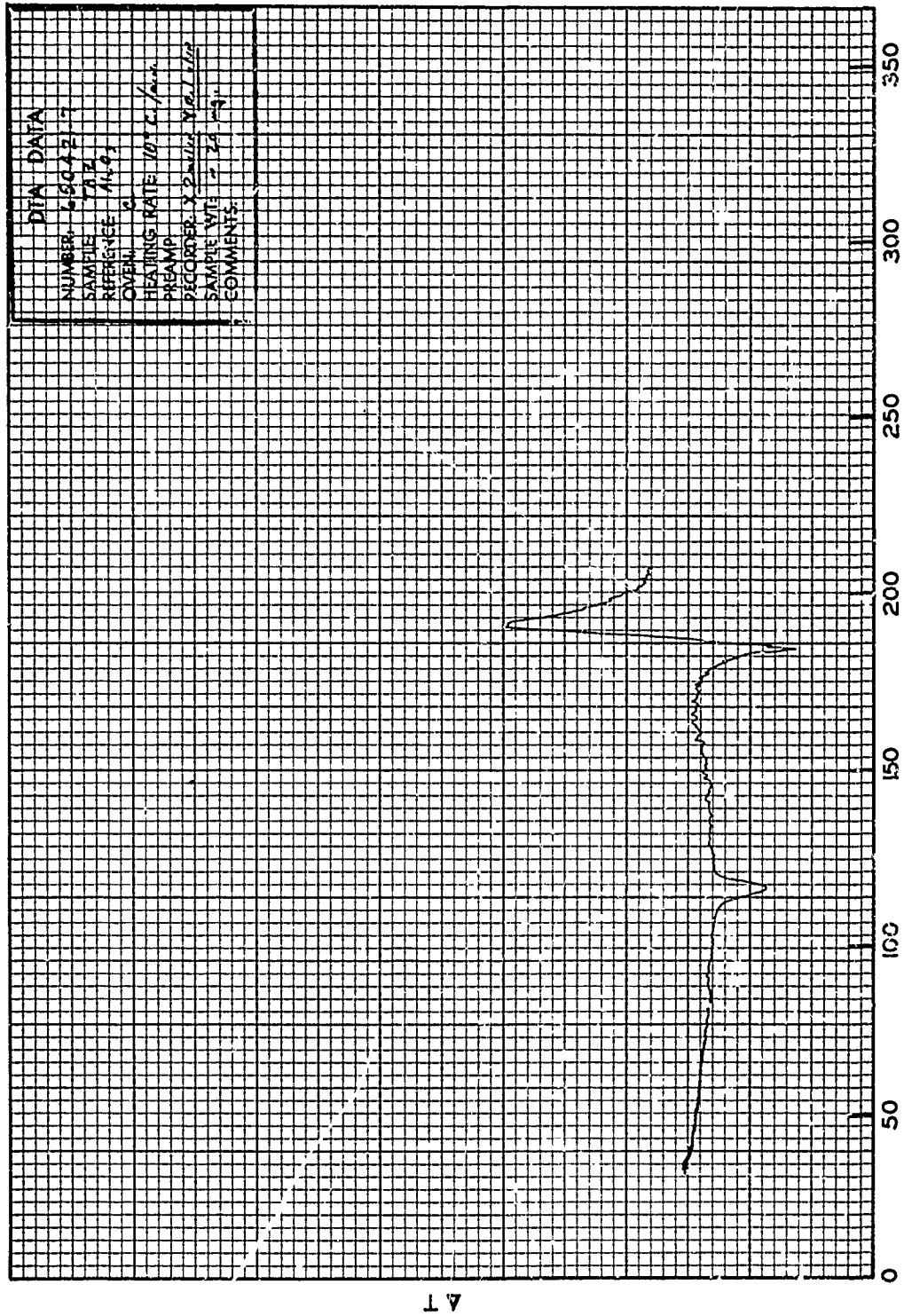
THERMOGRAM NO. 8



ΔT

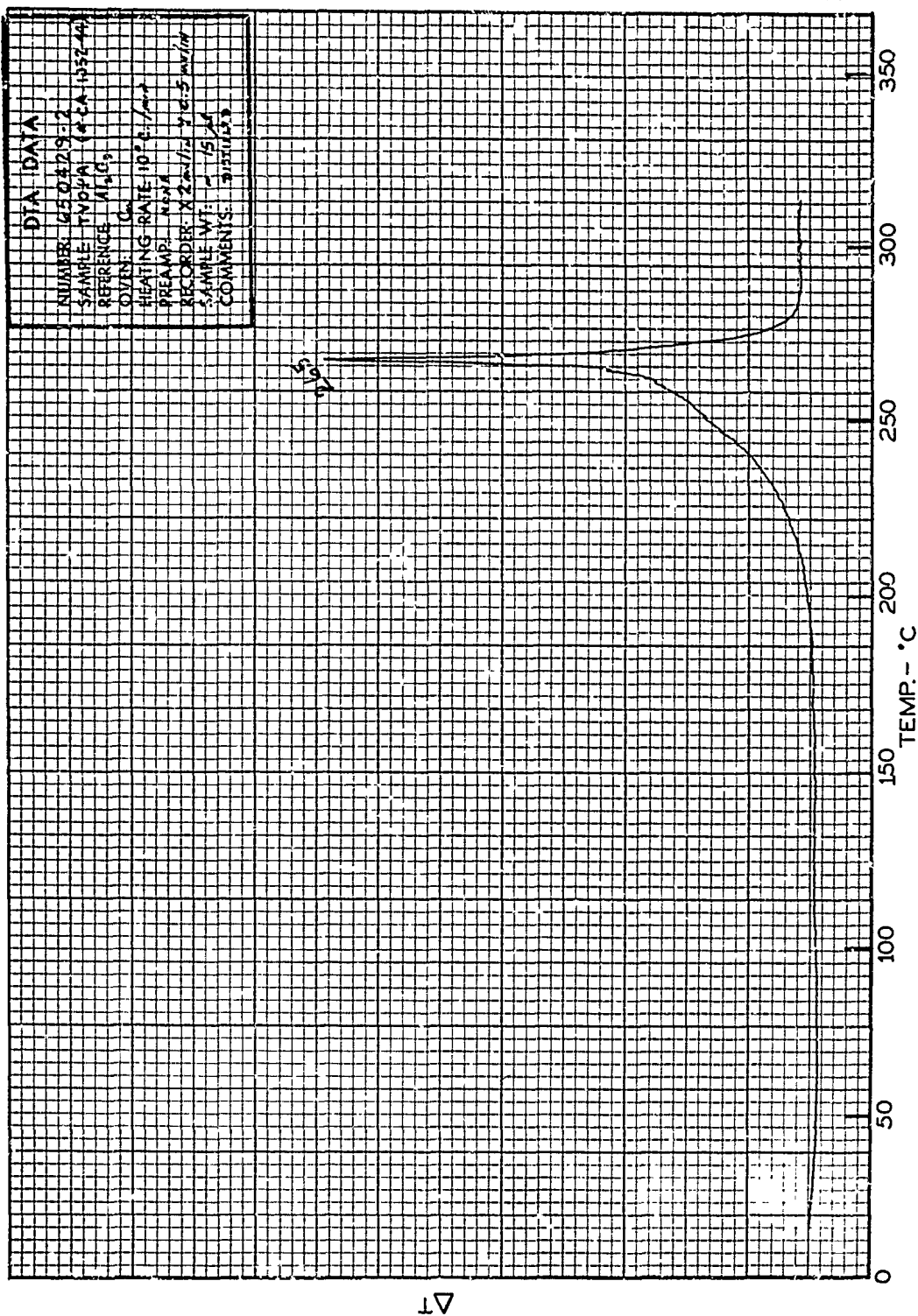
THERMOGRAM NO. 9

TAZ



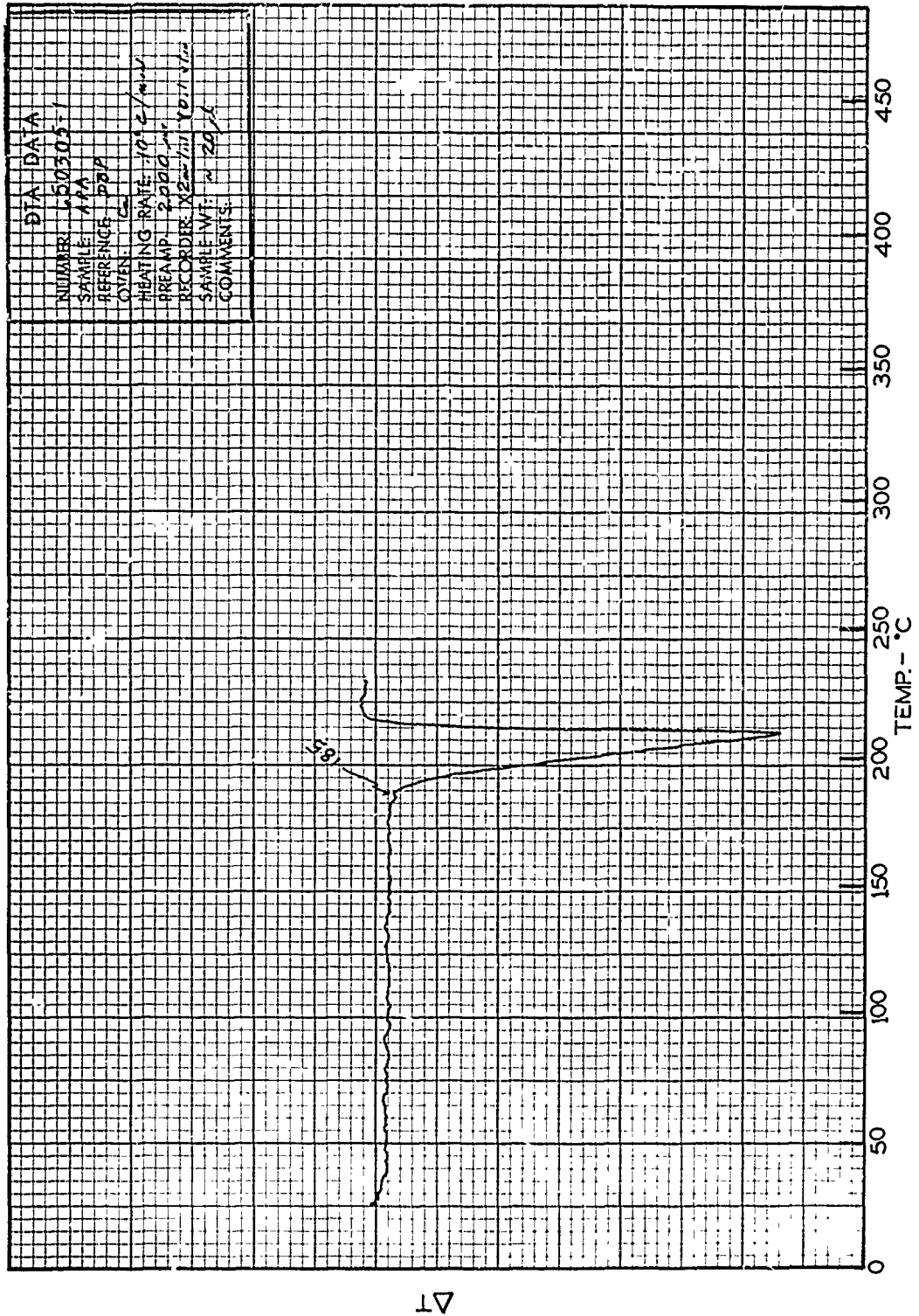
TVOPA

THERMOGRAM NO. 10



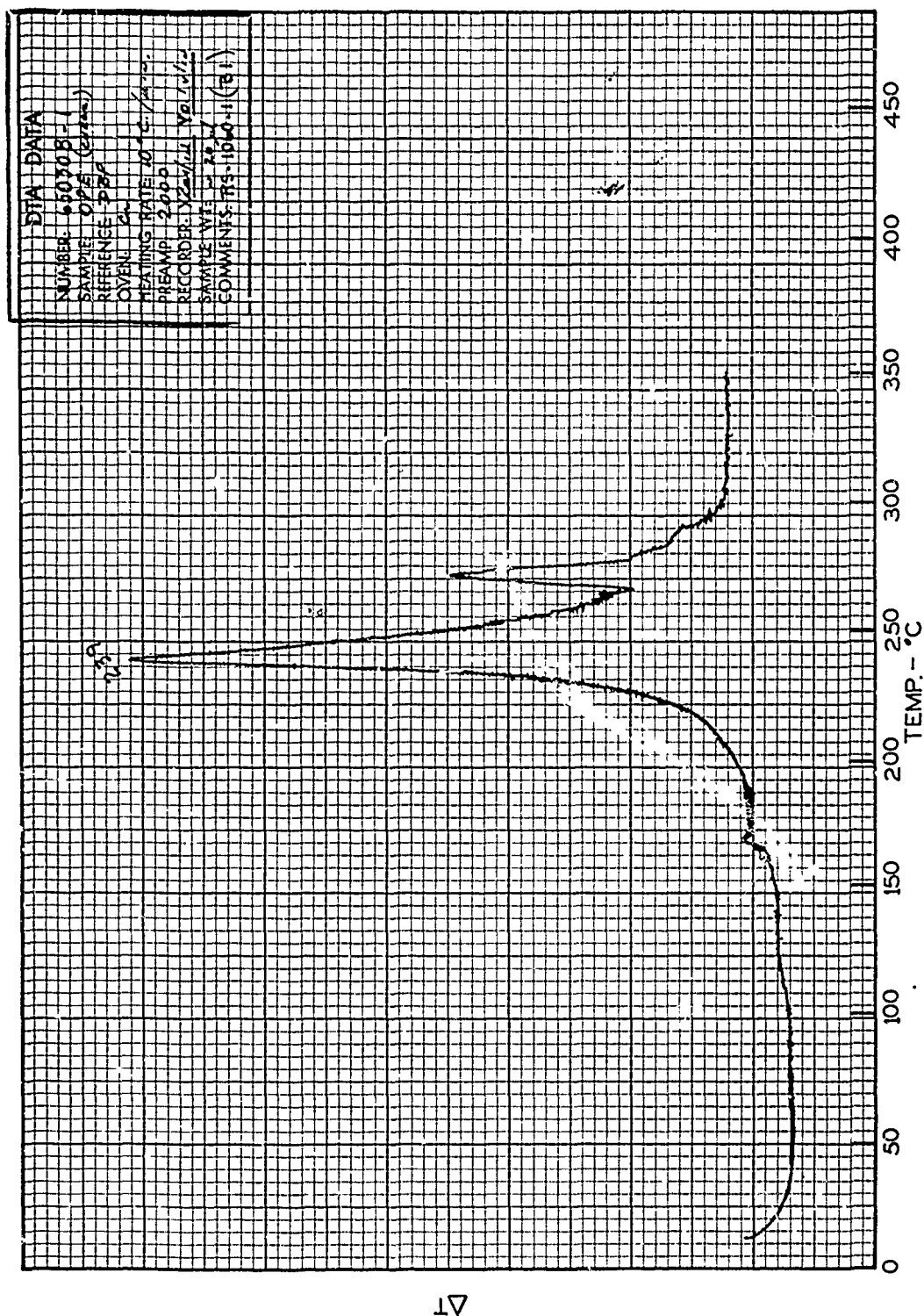
THERMOGRAM NO. II

APA



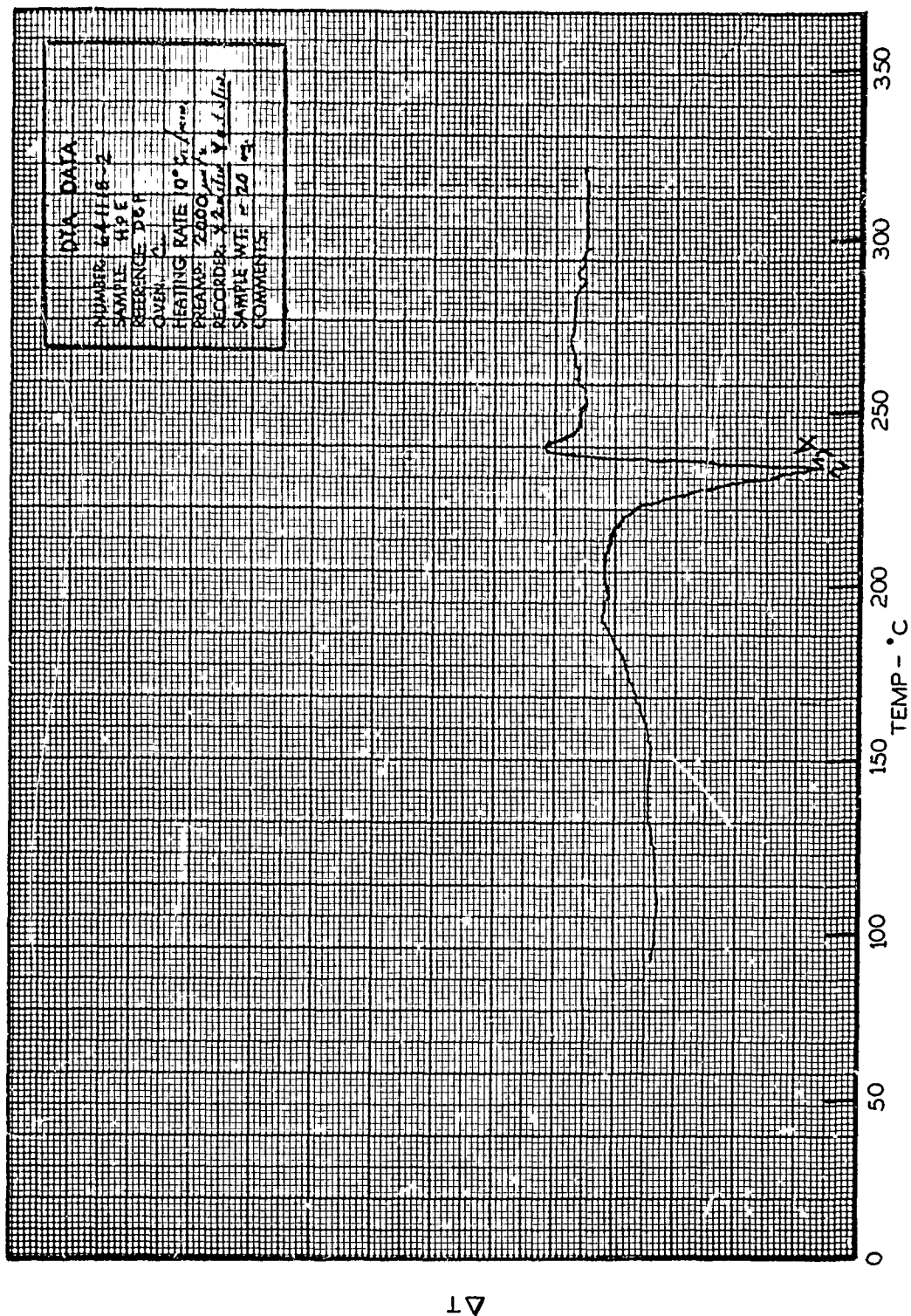
THERMOGRAM NO. 12

OPE



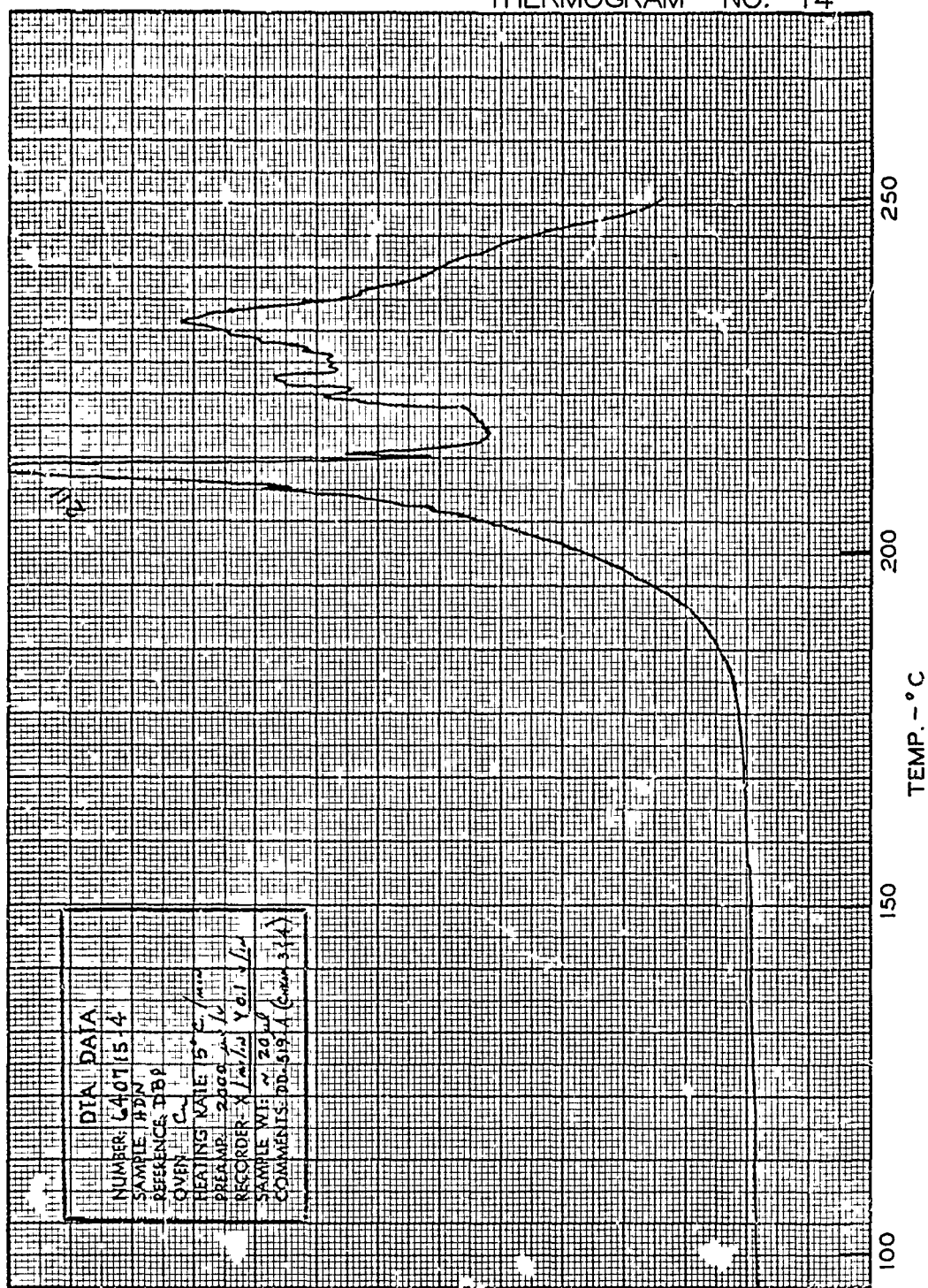
ΔT

HPE



THERMOGRAM NO. 14

HDN

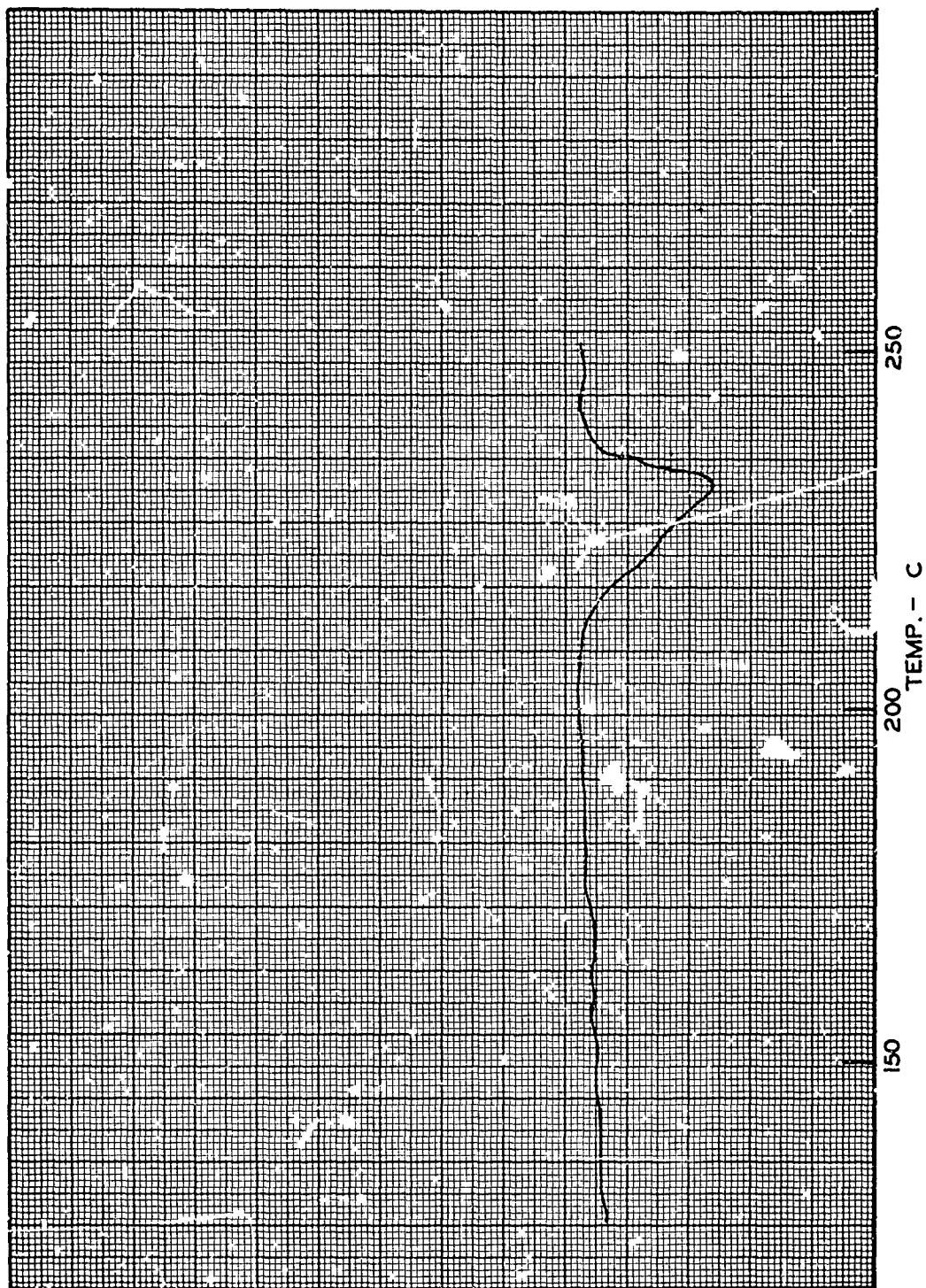


DTA DATA	
NUMBER	L40T15-4
SAMPLE	HDN
REFERENCE	DBP
OVEN	C
HEATING RATE	5°C/min
PREMP	2000
RECORD	1/20/73 Y6.1 J/L
SAMPLE WT	~20g
COMMENTS	DD-319.1 (Gross 314)

Δ T

THERMOGRAM NO. 15

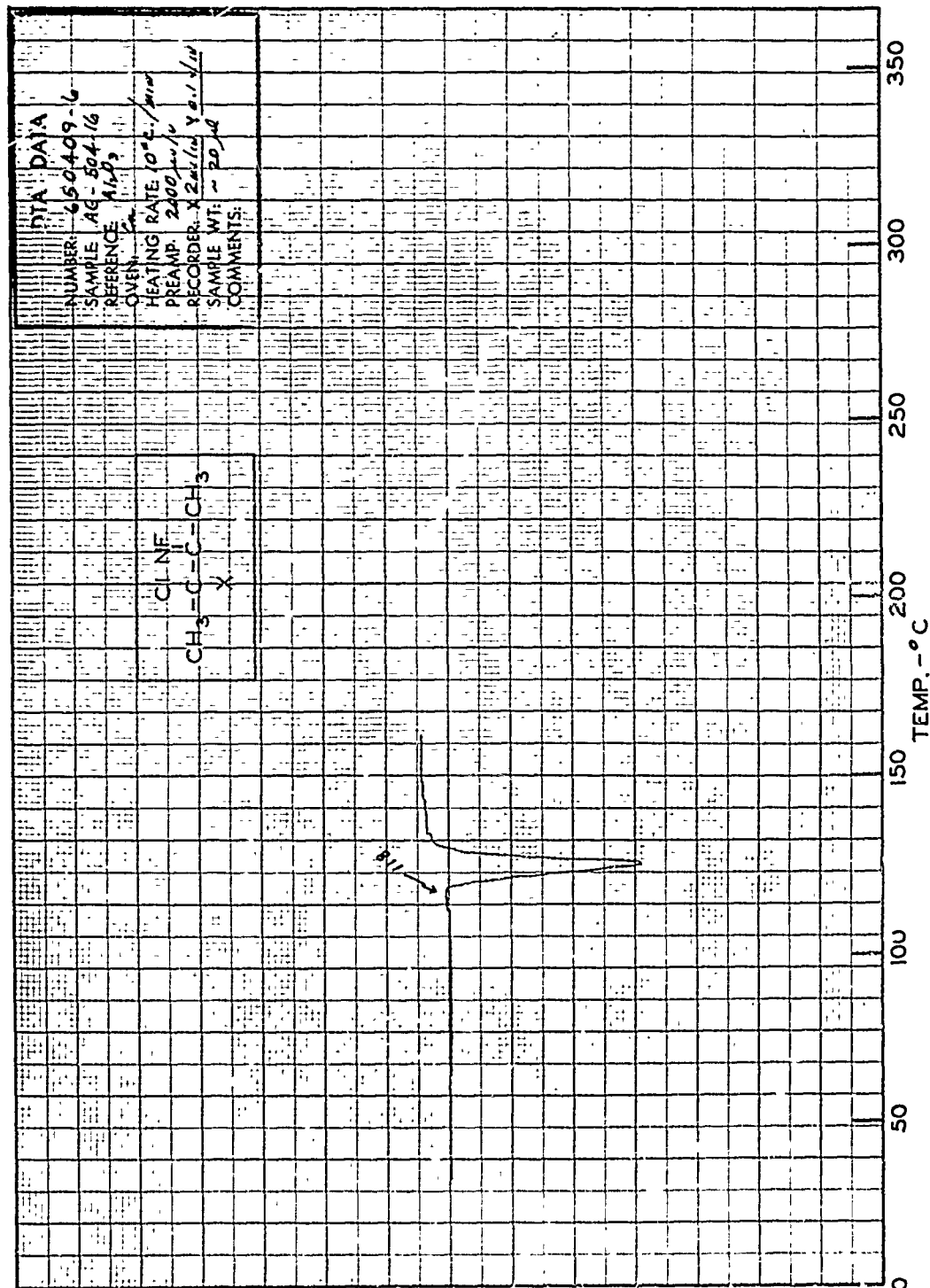
TNFH



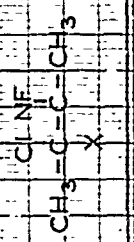
ΔT

THERMOGRAM NO. 16

MNFP

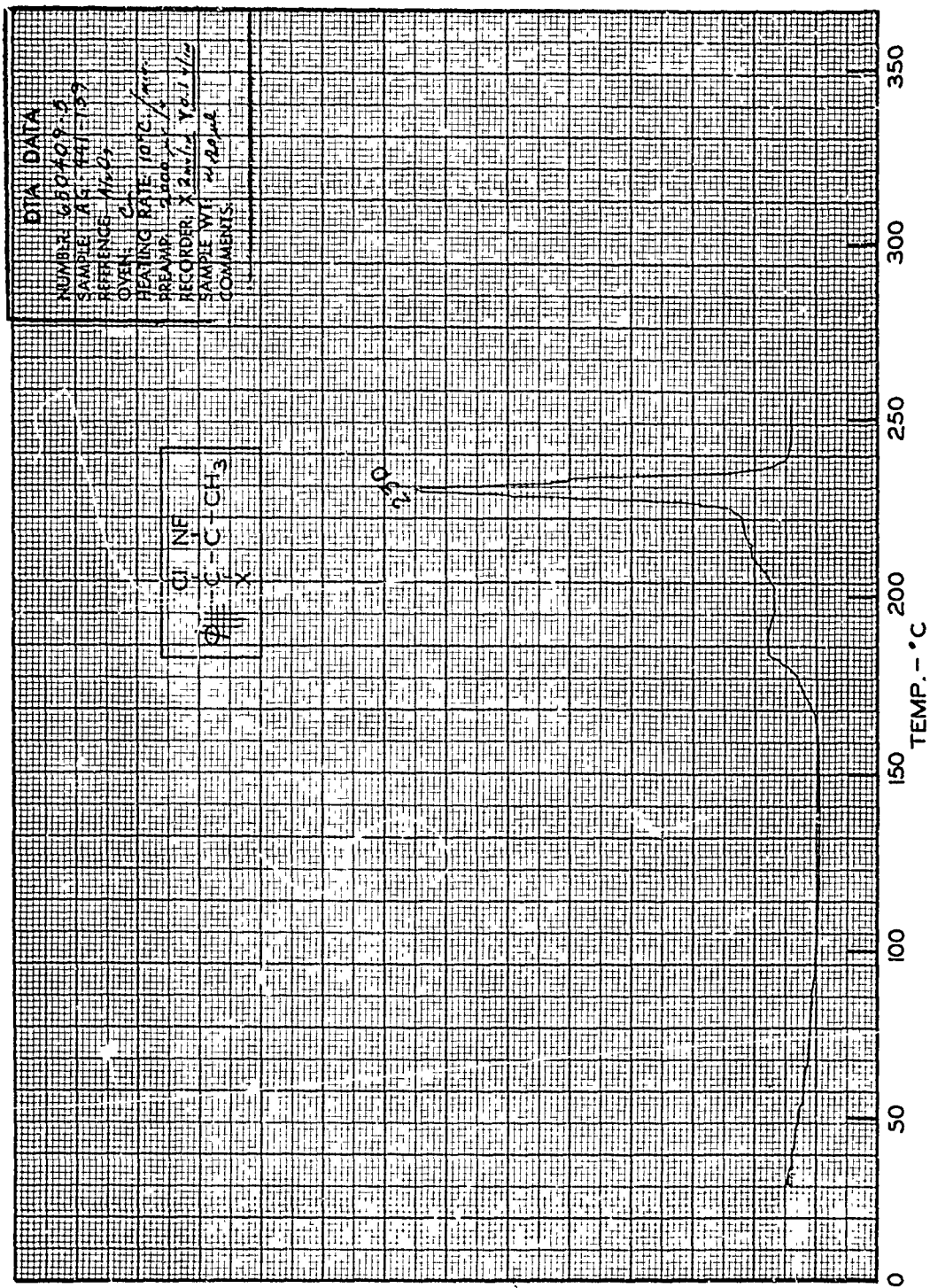


DTA DATA
 NUMBER: 650409-6
 SAMPLE: Ag-504-16
 REFERENCE: Al_2O_3
 HEATING RATE: 10 °C./min
 PREAMP: 200 μV
 RECORDER: X 2 sec/cm Y 0.1 $\mu V/in$
 SAMPLE WT: ~ 20 μg
 COMMENTS:



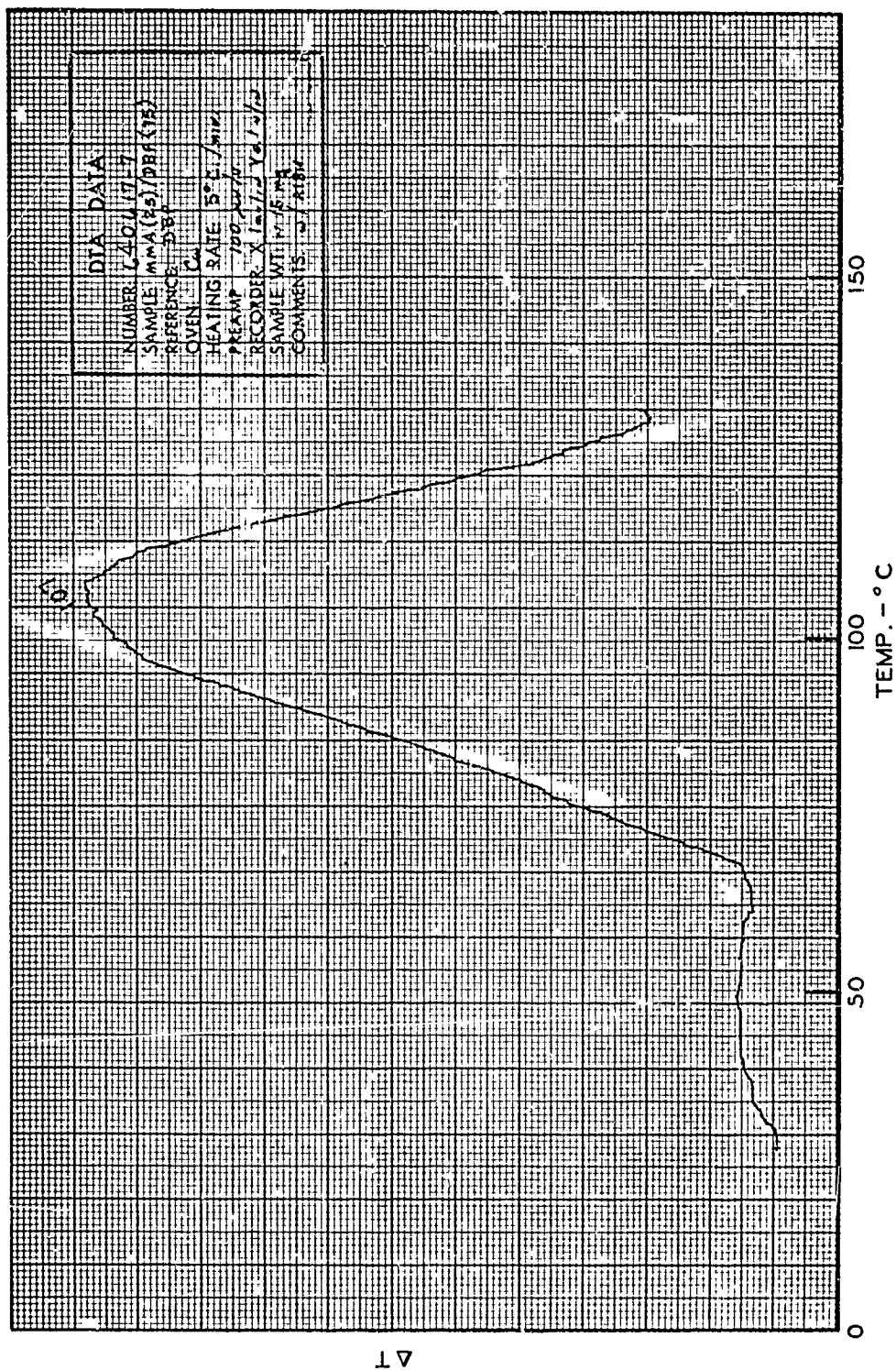
THERMOGRAM NO. 17

PNFP



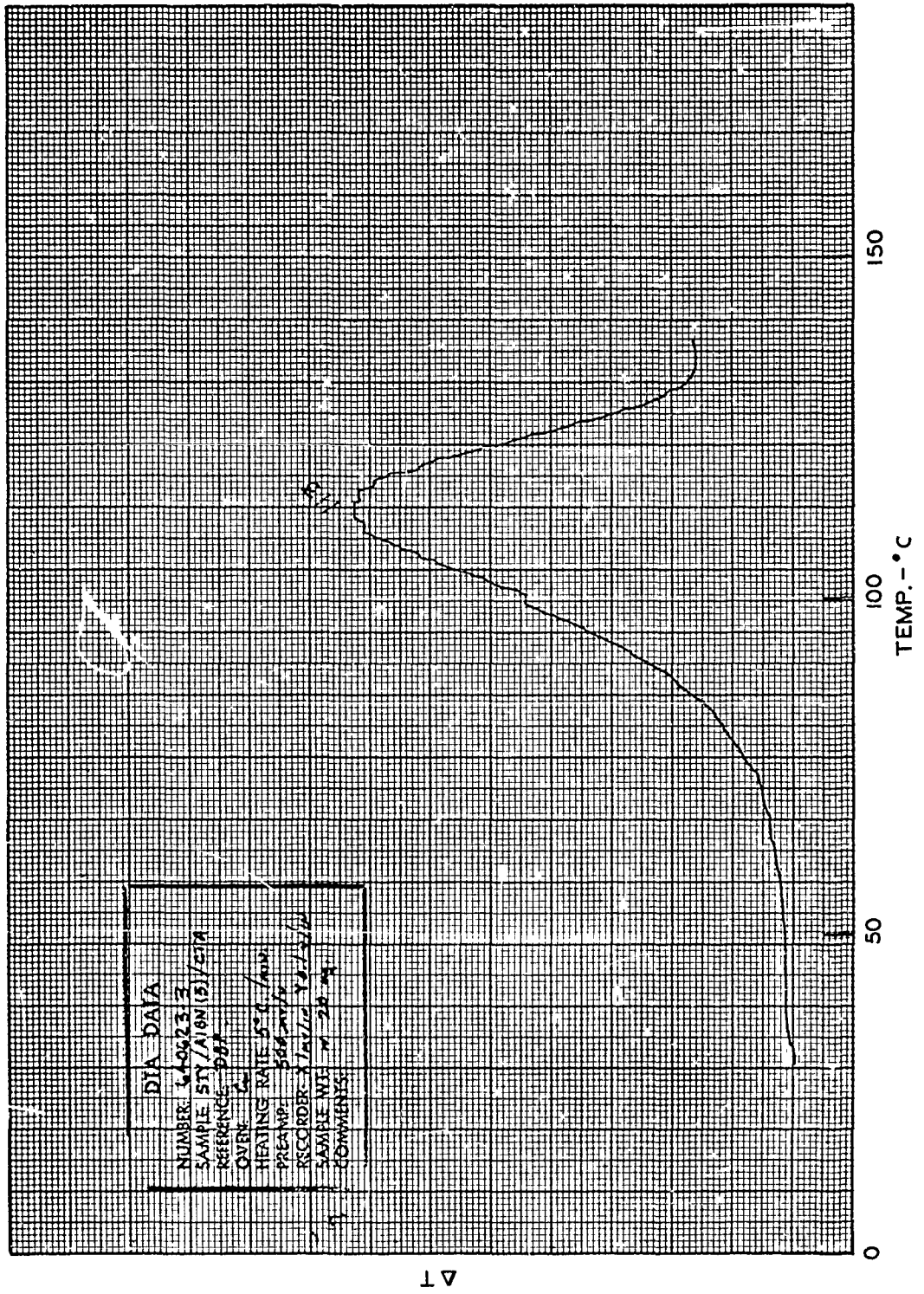
THERMOGRAM NO. 18

m-MMA



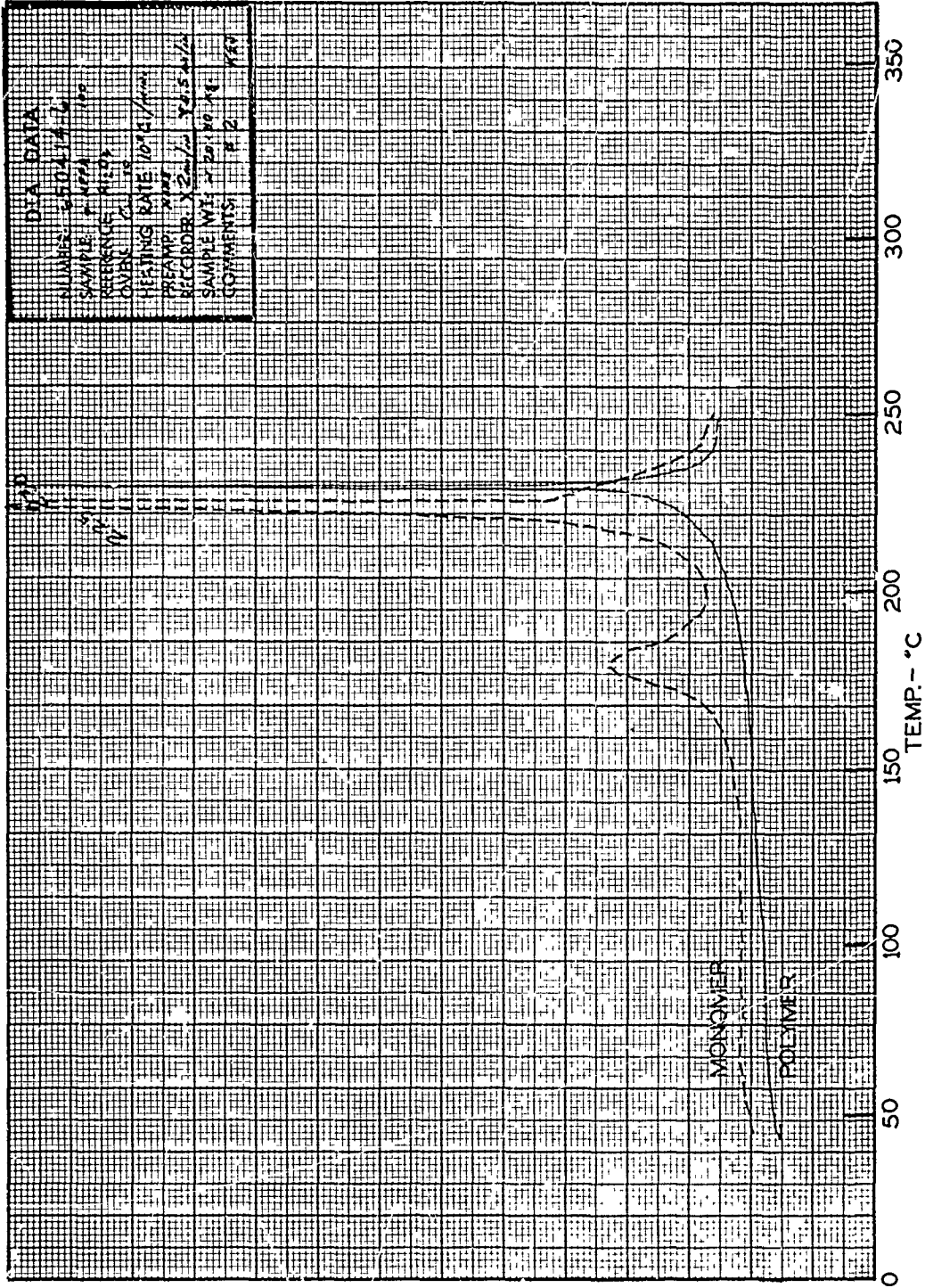
THERMOGRAM NO. 19

m-STY



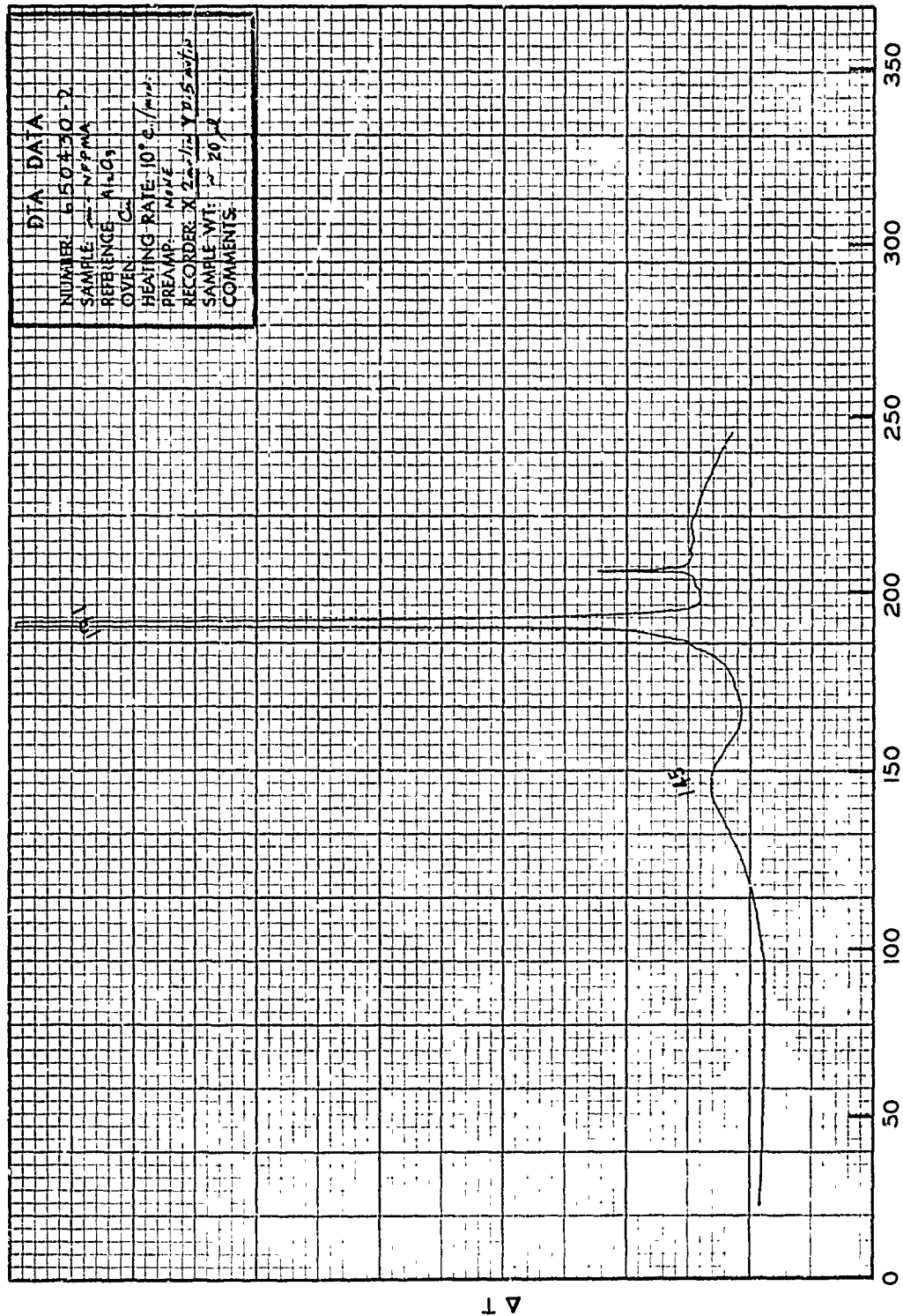
THERMOGRAM NO. 21

p-NFPA

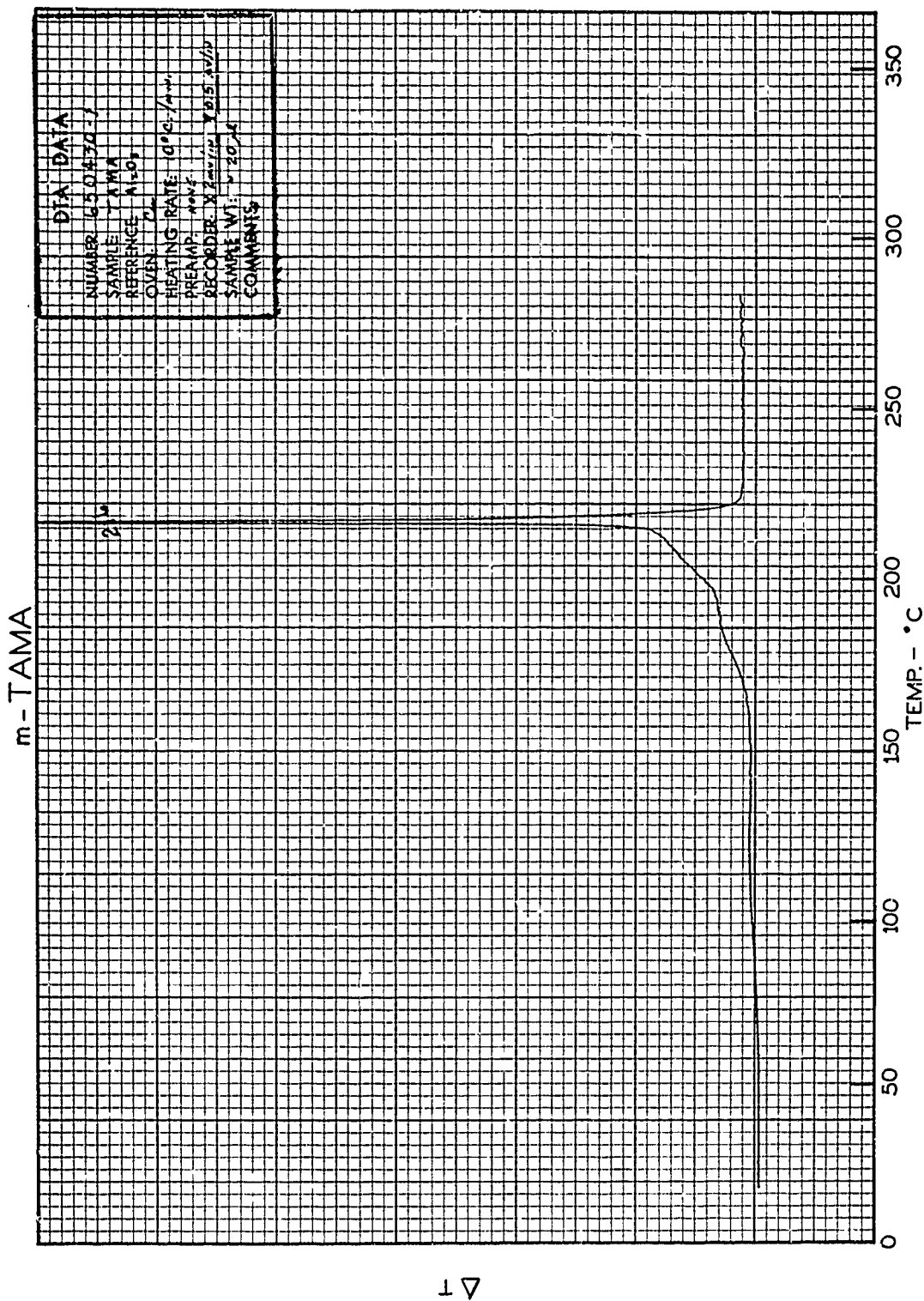


THERMOGRAM NO. 22

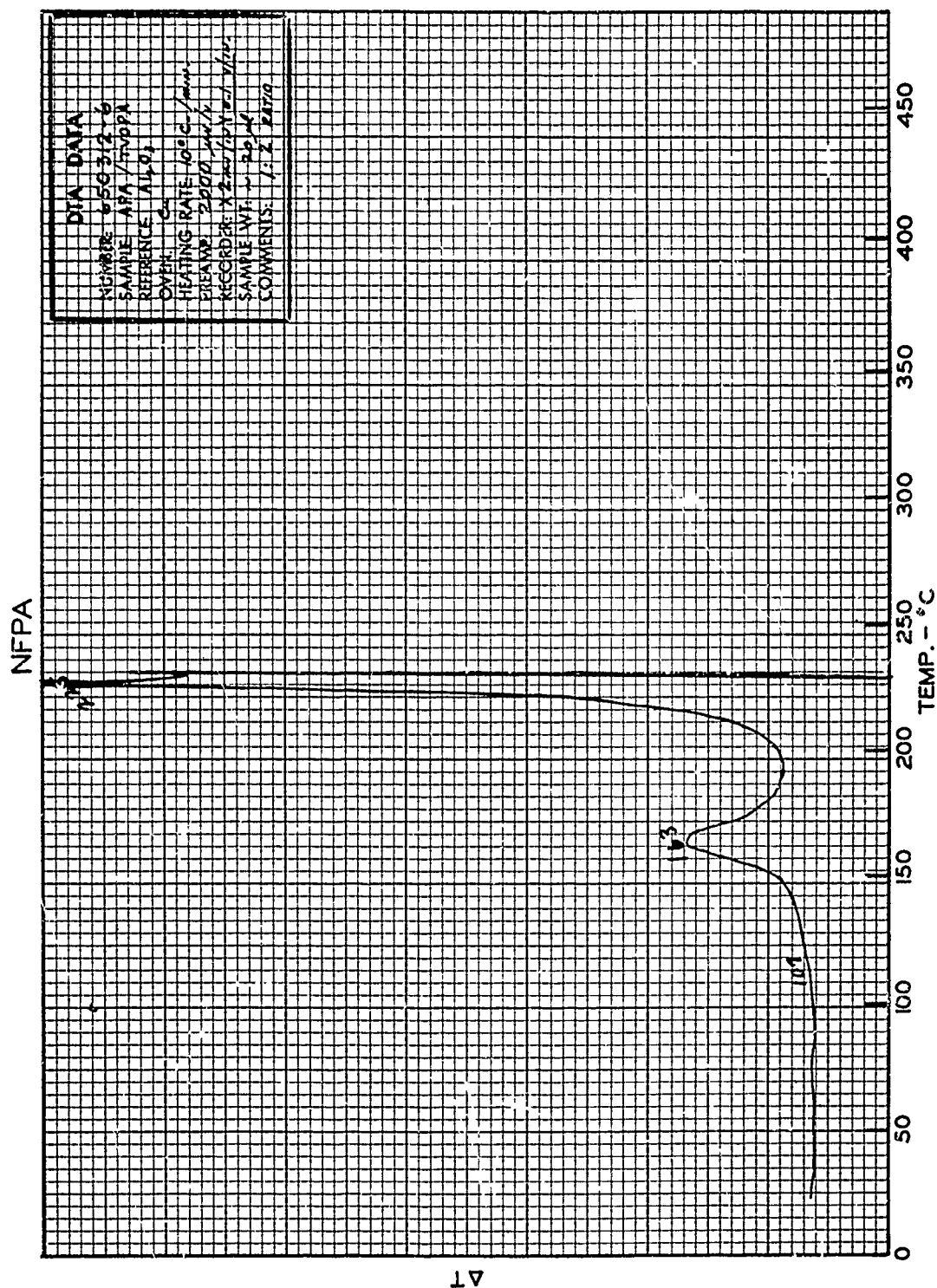
m - NFPMA



THERMOGRAM NO. 23

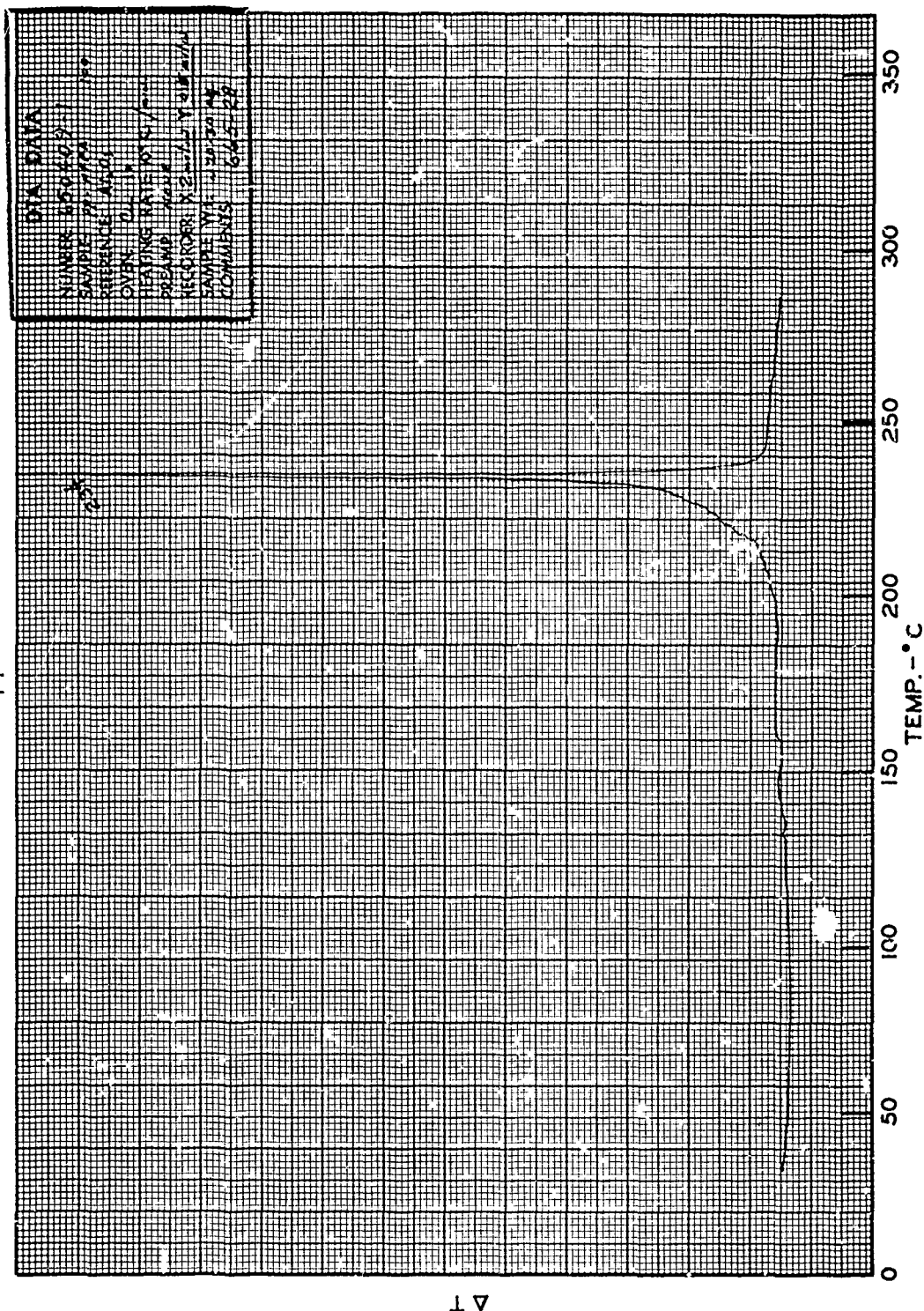


THERMOGRAM NO. 24



THERMOGRAM NO. 25

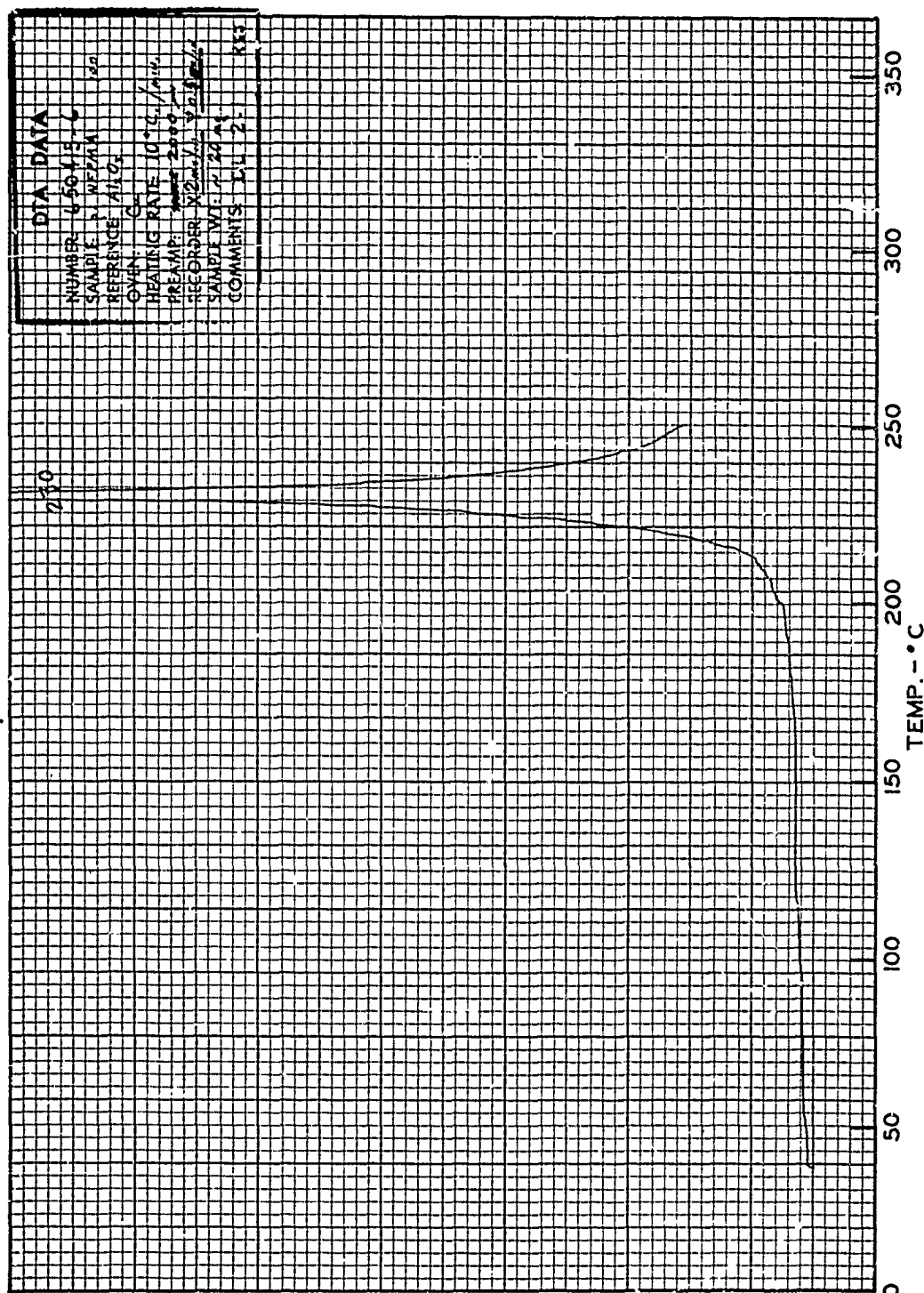
pp - NFPA



ΔT

THERMOGRAPH NO. 26

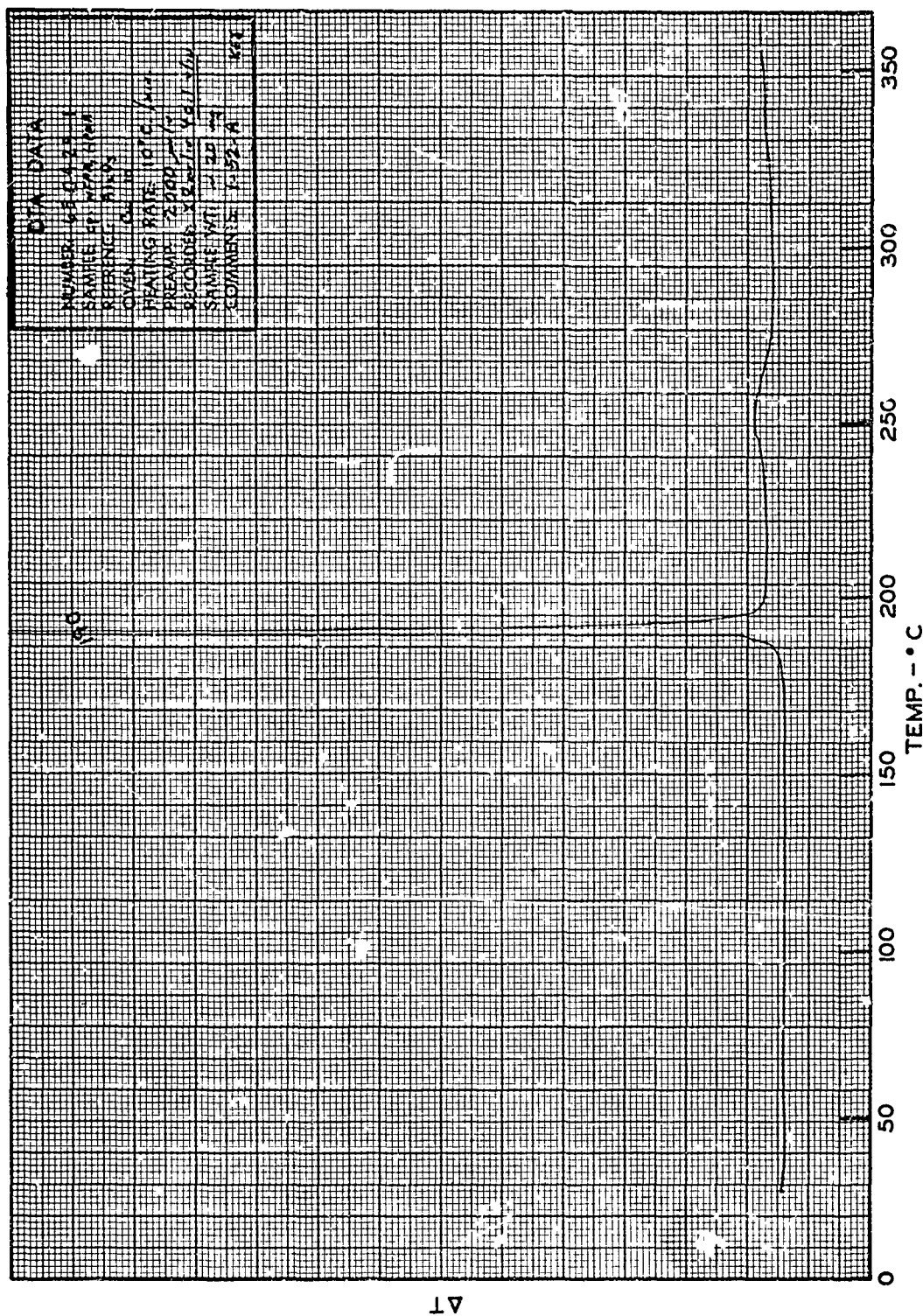
p - NFPMA



ΔT

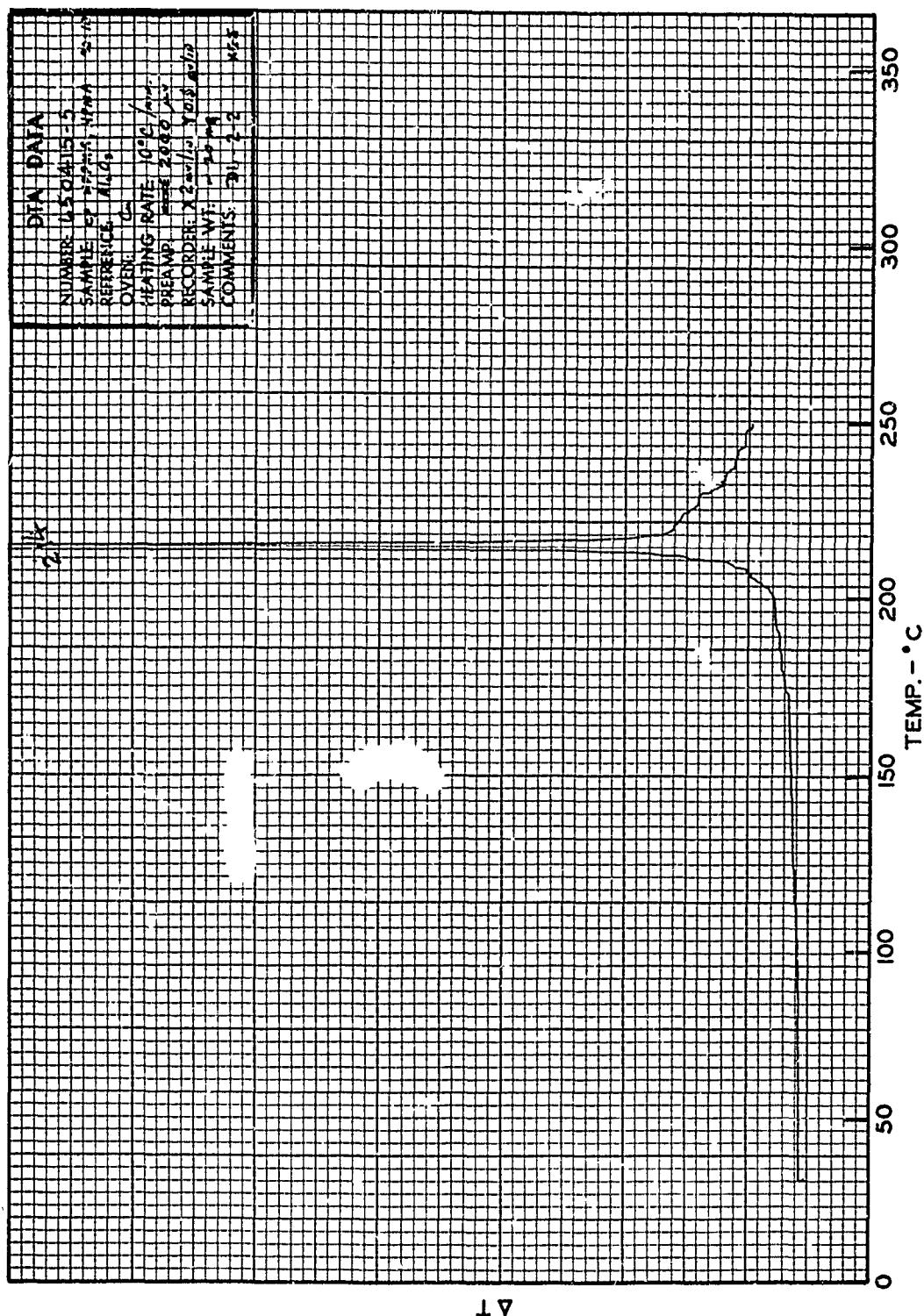
cp-NFPA, HPMA

THERMOGRAM NO. 27



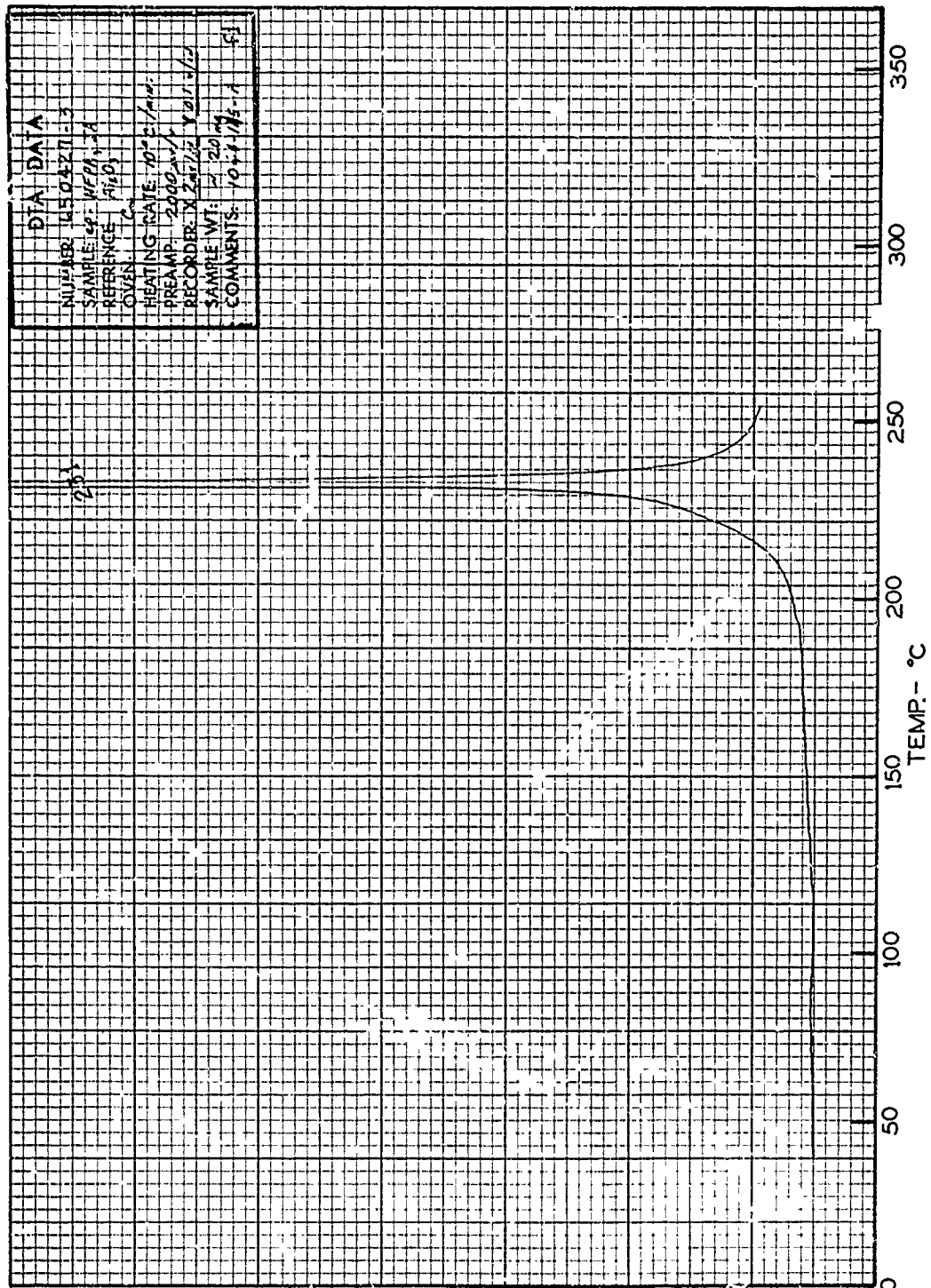
cp - NFPMA , HPMA

THERMOGRAM NO. 28



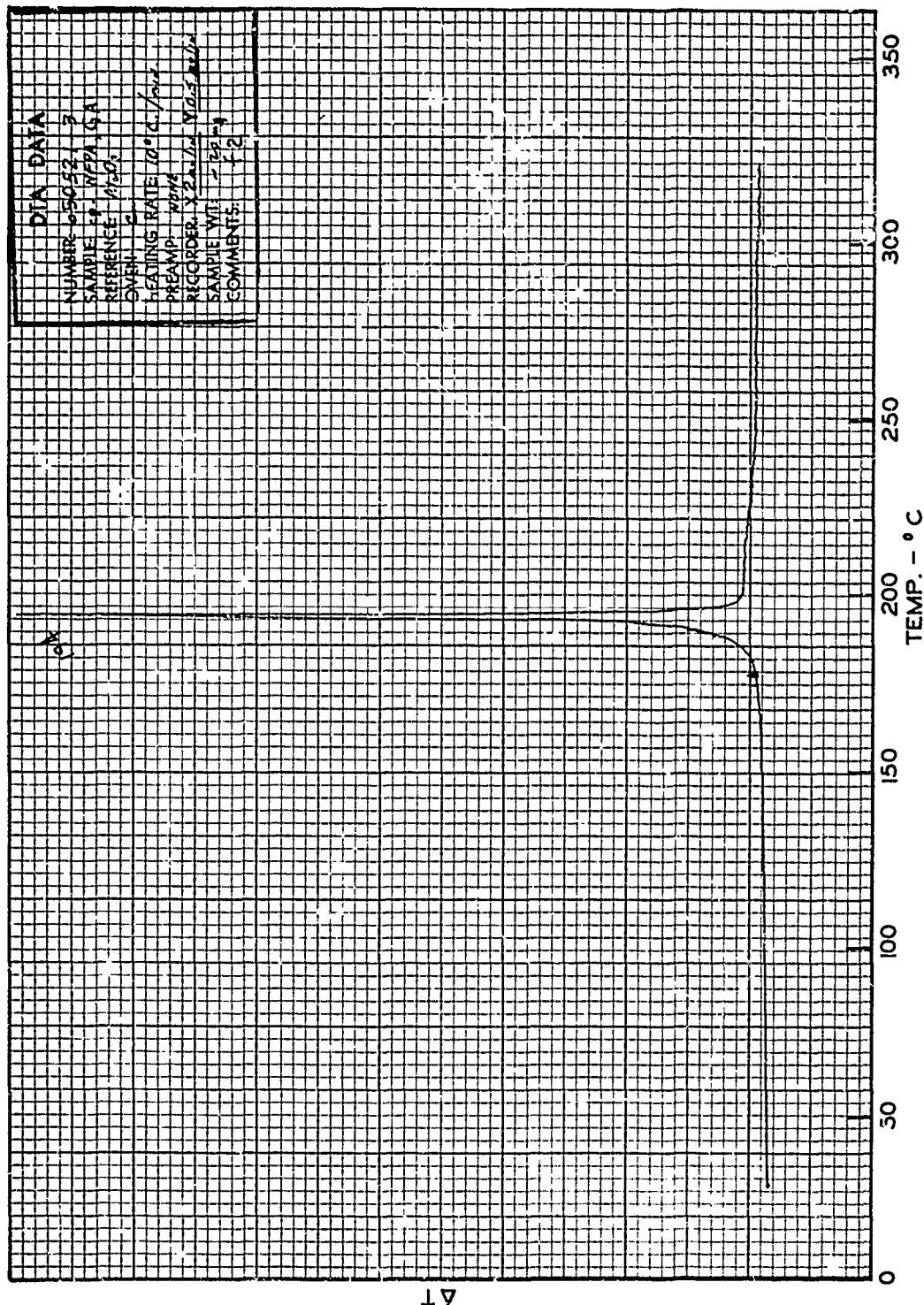
cp - NFPA, IA

THERMOGRAM NO. 29



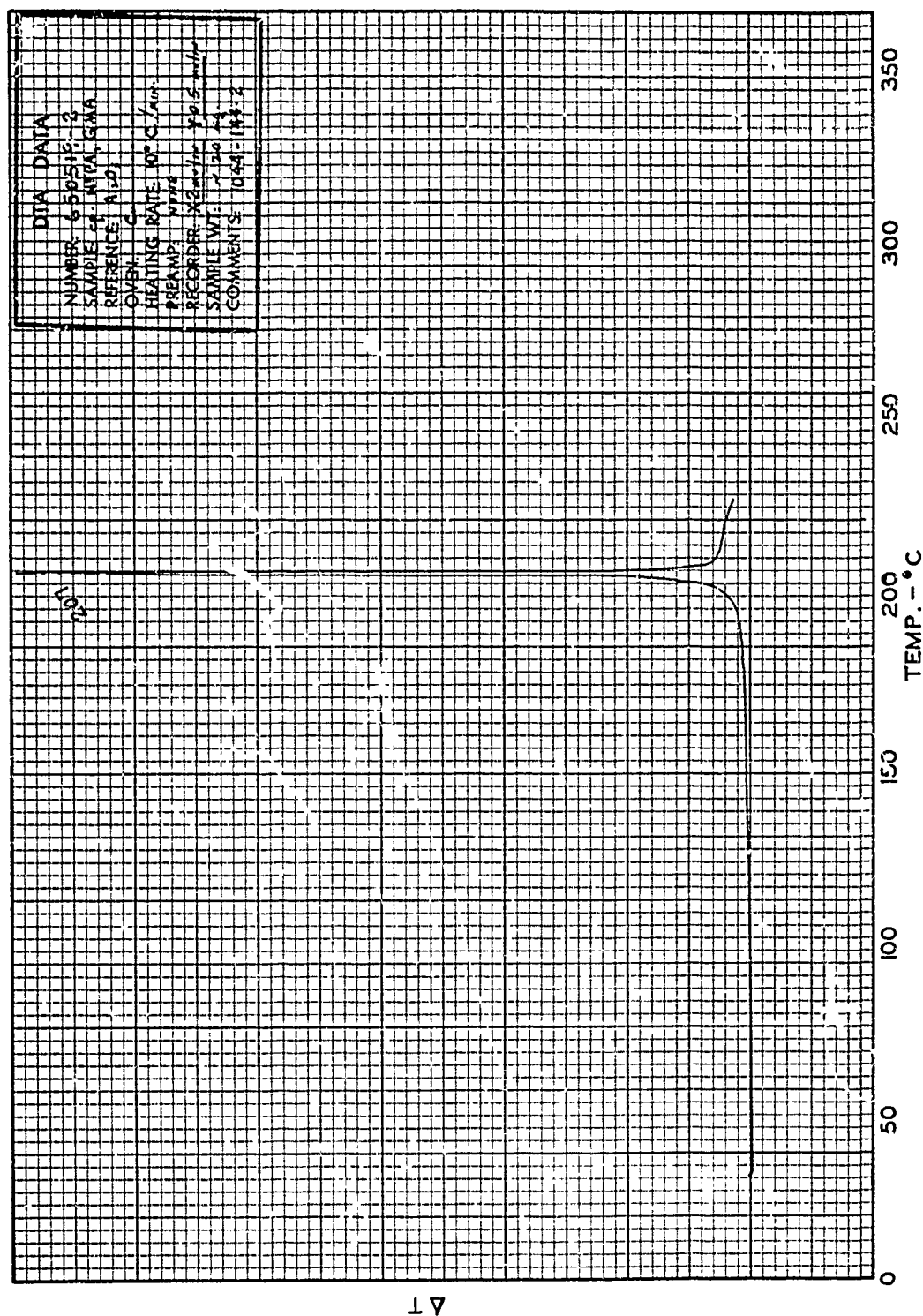
THERMOGRAM NO. 30

cp-NFPA, GA

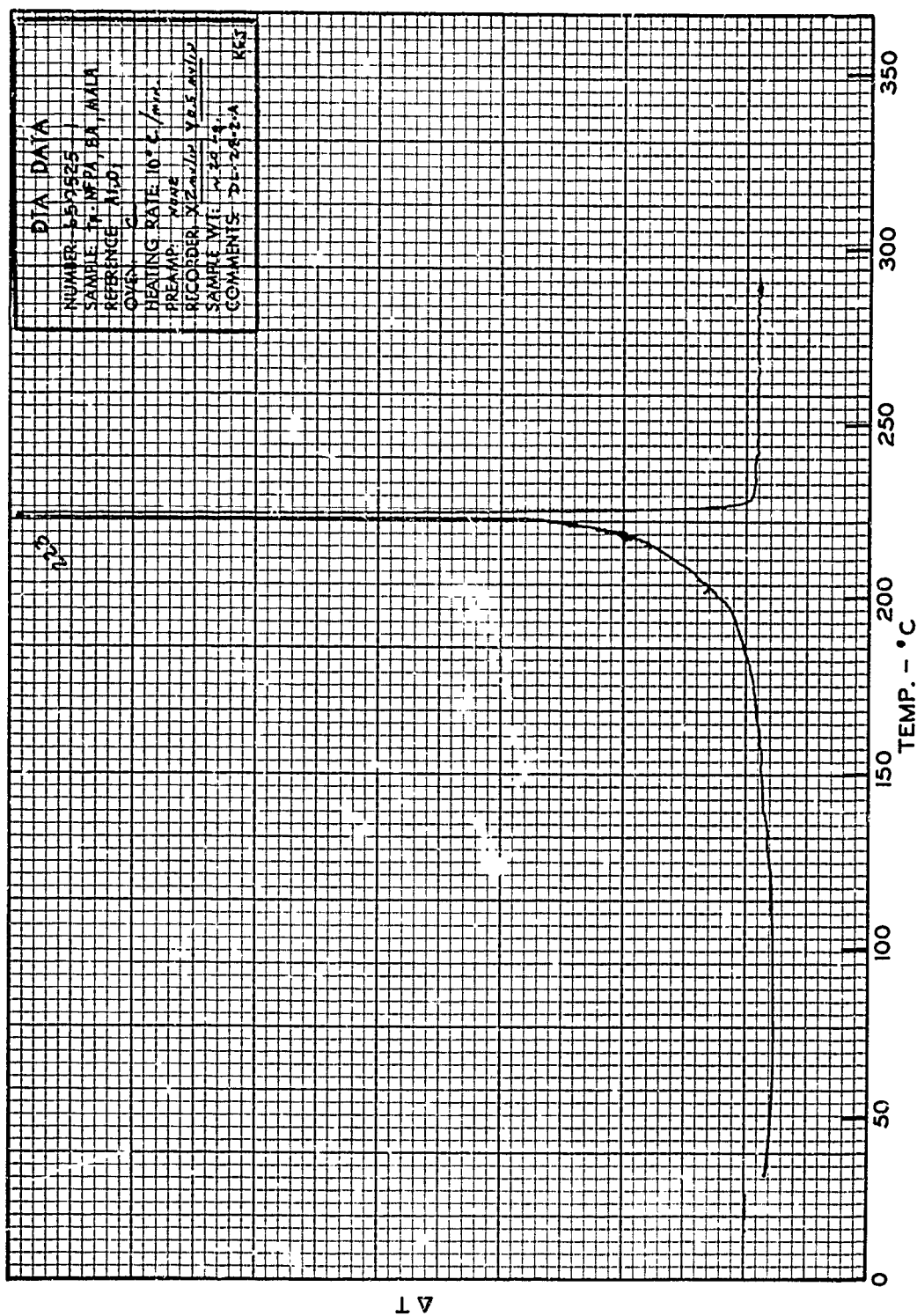


THERMOGRAM NO. 31

cp-NFPA, GMA

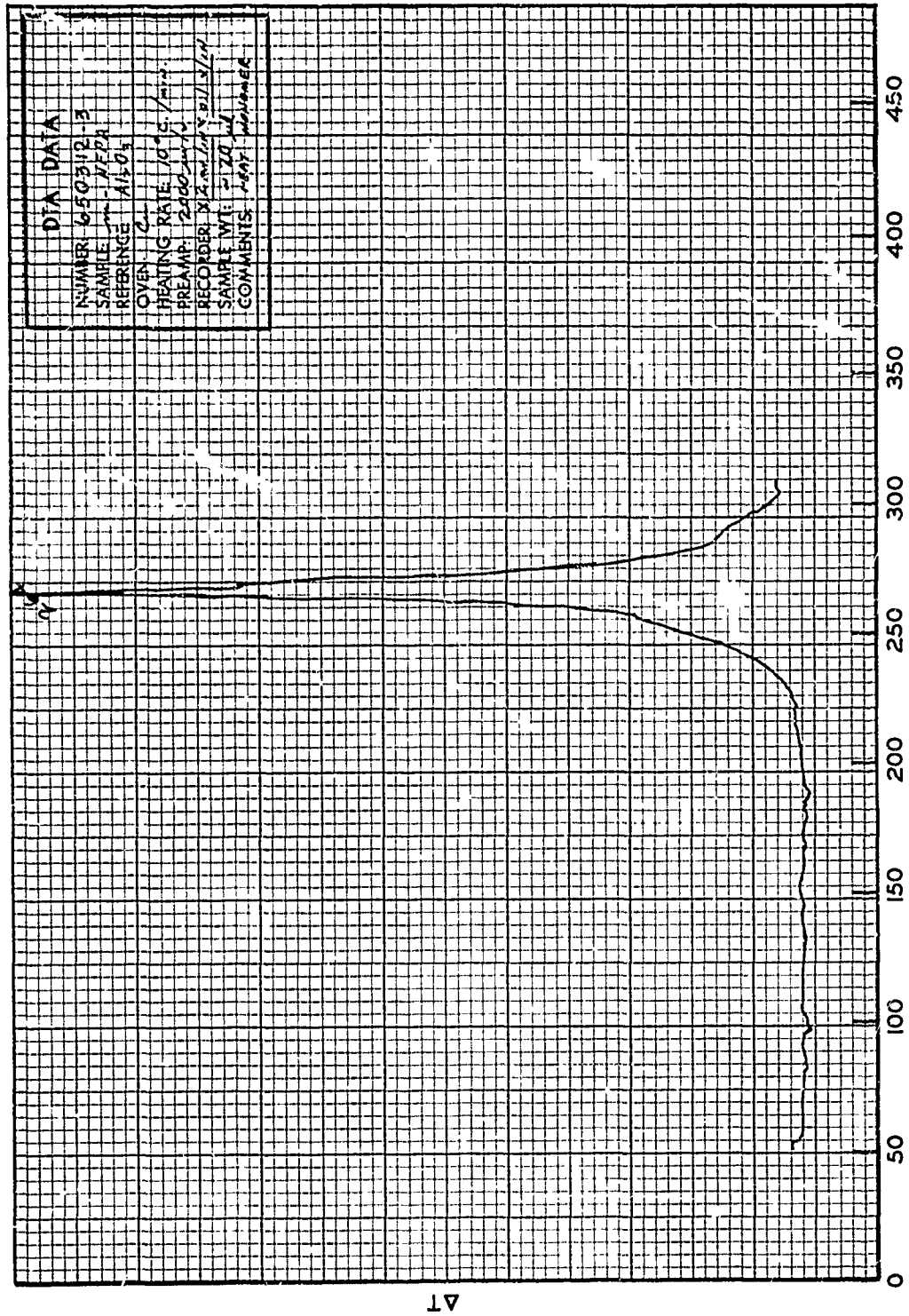


tp-NFPA, BA, MALA



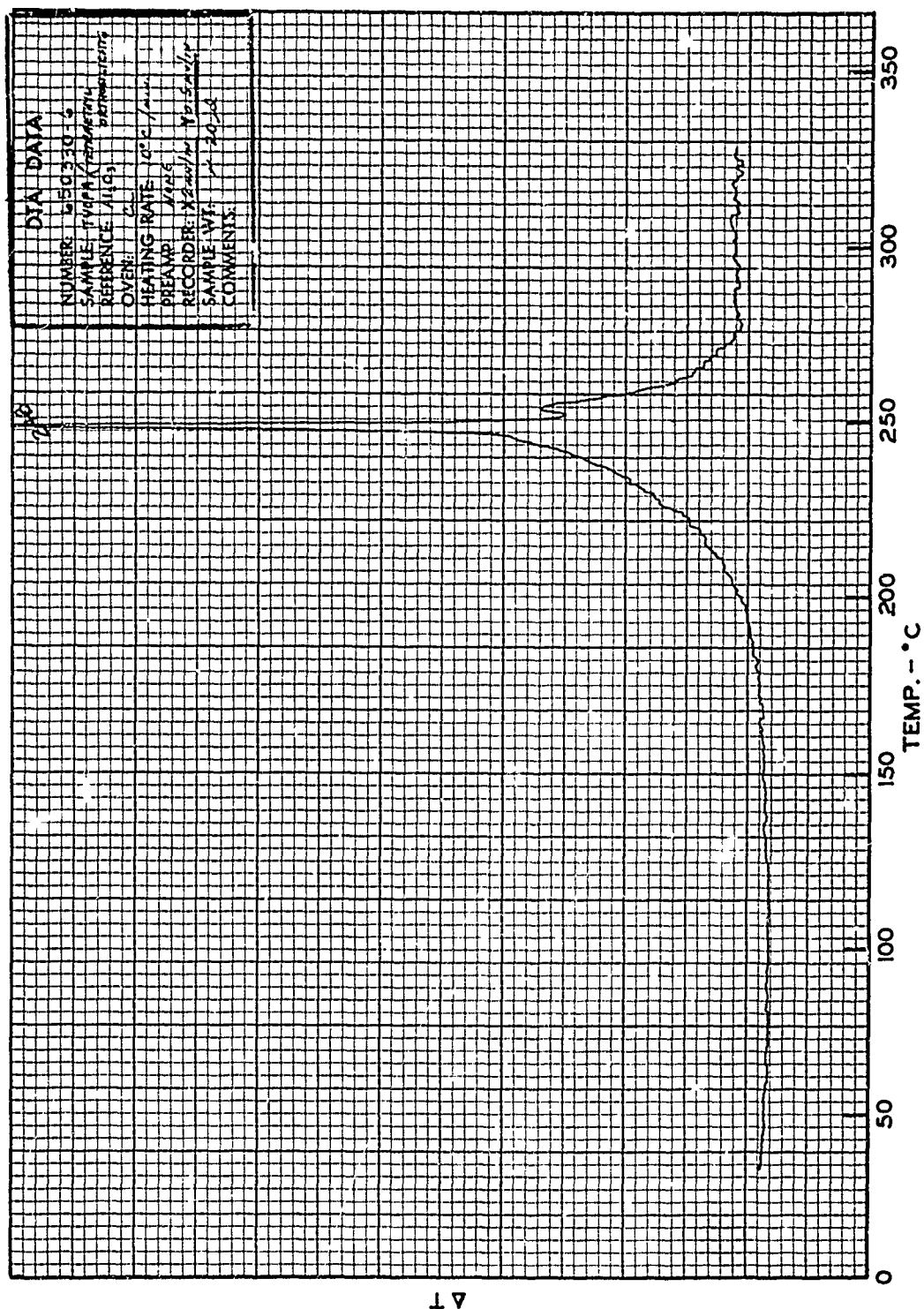
THERMOGRAM NO. 33

TVOPA/APA



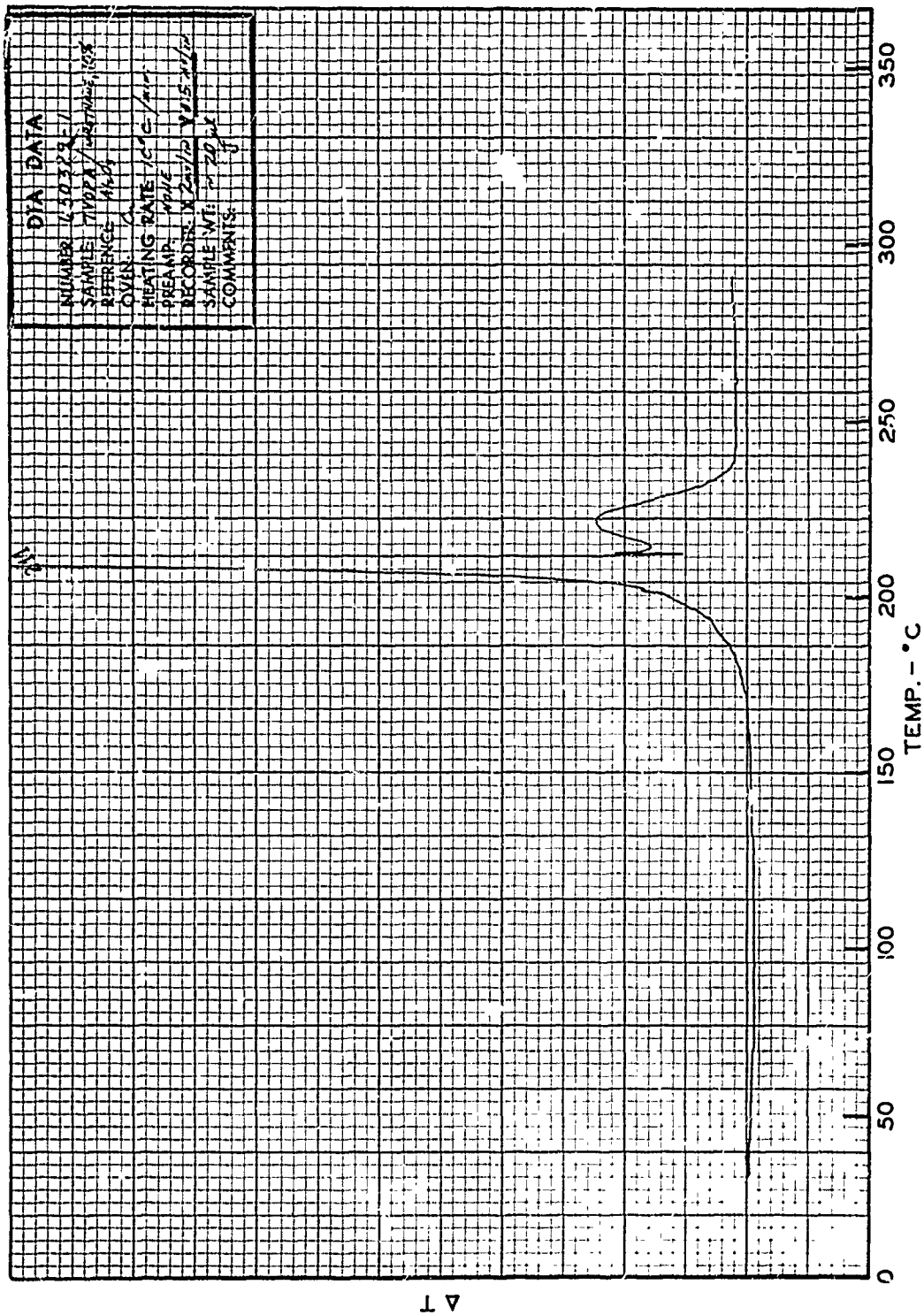
DTA DATA
 NUMBER 650312-3
 SAMPLE TVOPA
 REFERENCE A1505
 OVEN 12
 HEATING RATE 10°C/min
 PREAMP 2000mV
 RECORDED 12 mV 11/13/74
 SAMPLE WT: 2.70 g
 COMMENTS: 1st run, 1st run

TVOPA/TEOS



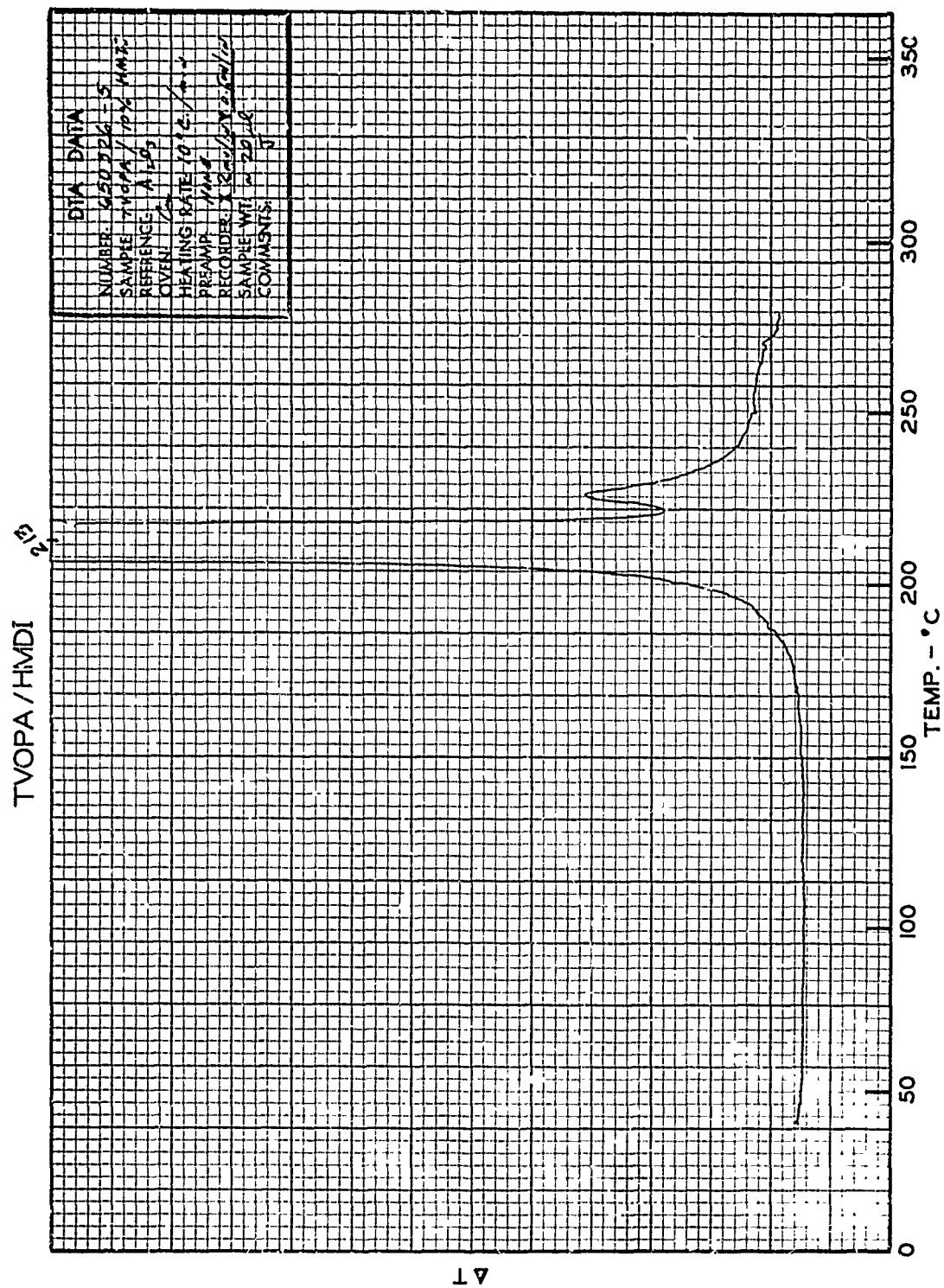
TVOPA / URETHANE

THERMOGRAM NO. 35



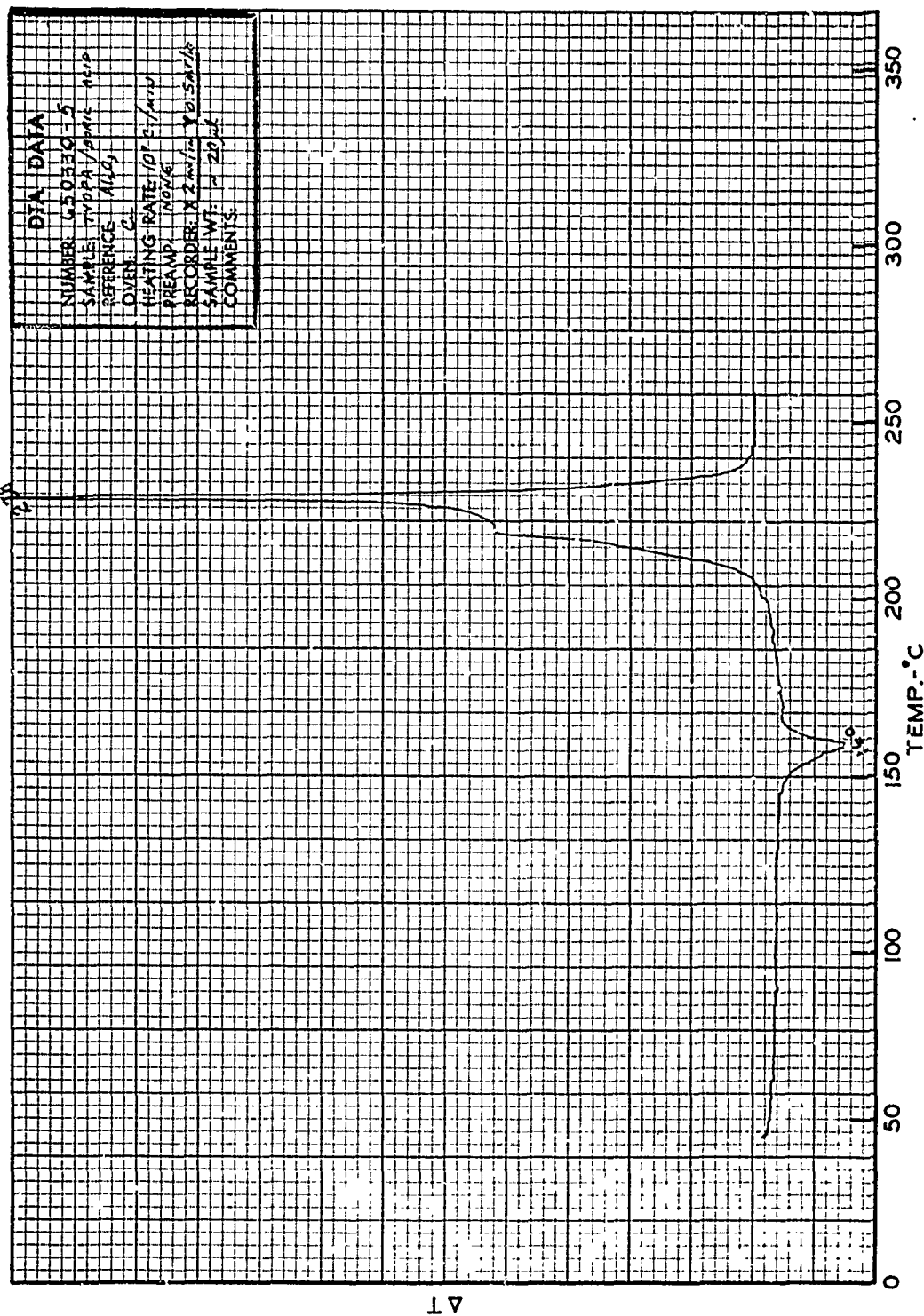
DTA DATA
 NUMBER: 630329-1
 SAMPLE: TVOPA / URETHANE-105
 REFERENCE: N/A
 OVEN: 2
 HEATING RATE: 10°C/min
 PREA MP: N/A
 RECORDS: 123/123 V015 N/A
 SAMPLE WT: 20.00 g
 COMMENTS:

THERMOGRAM NO. 36



THERMOGRAM NO. 37

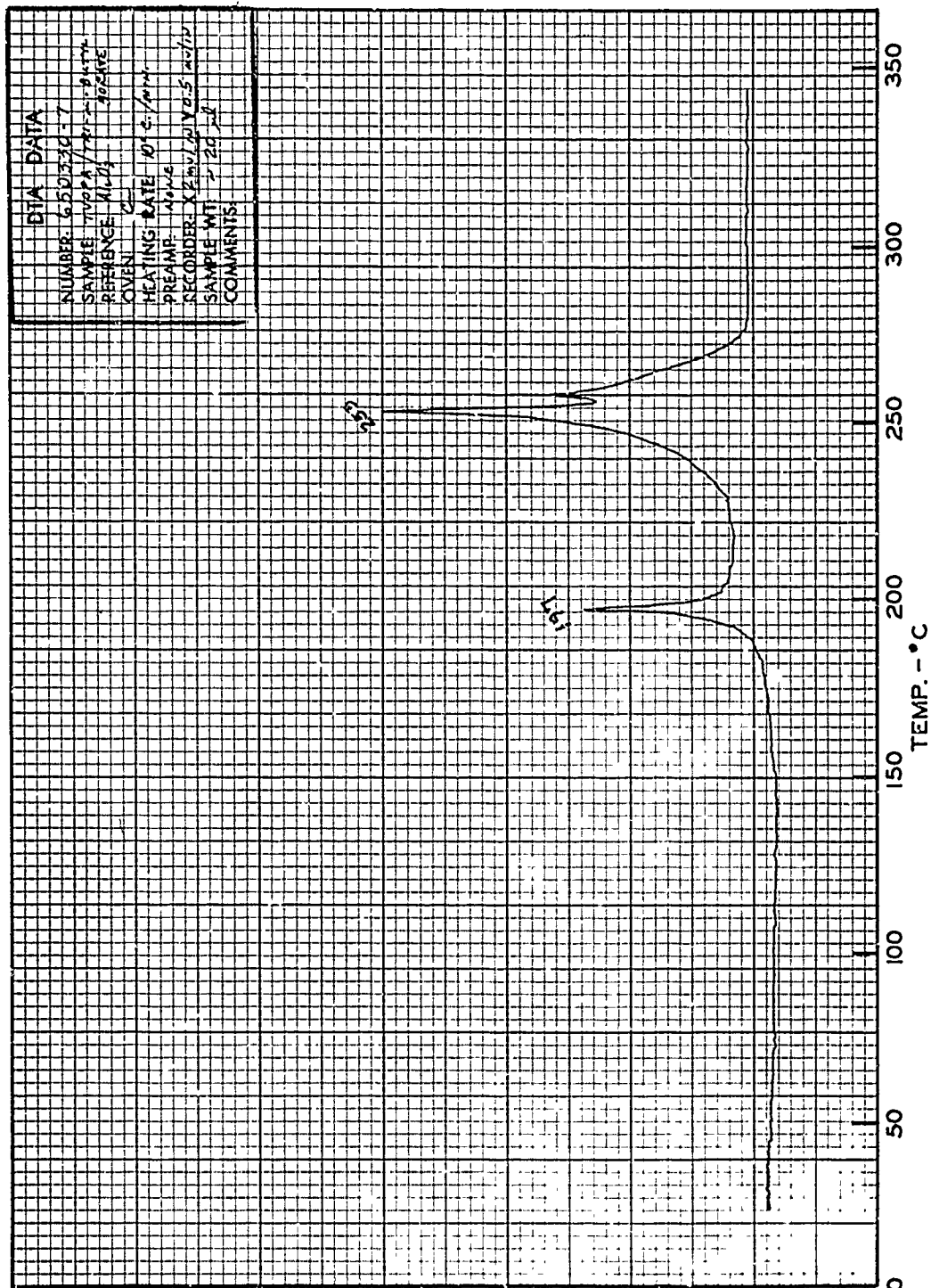
TVOPA / BORIC ACID



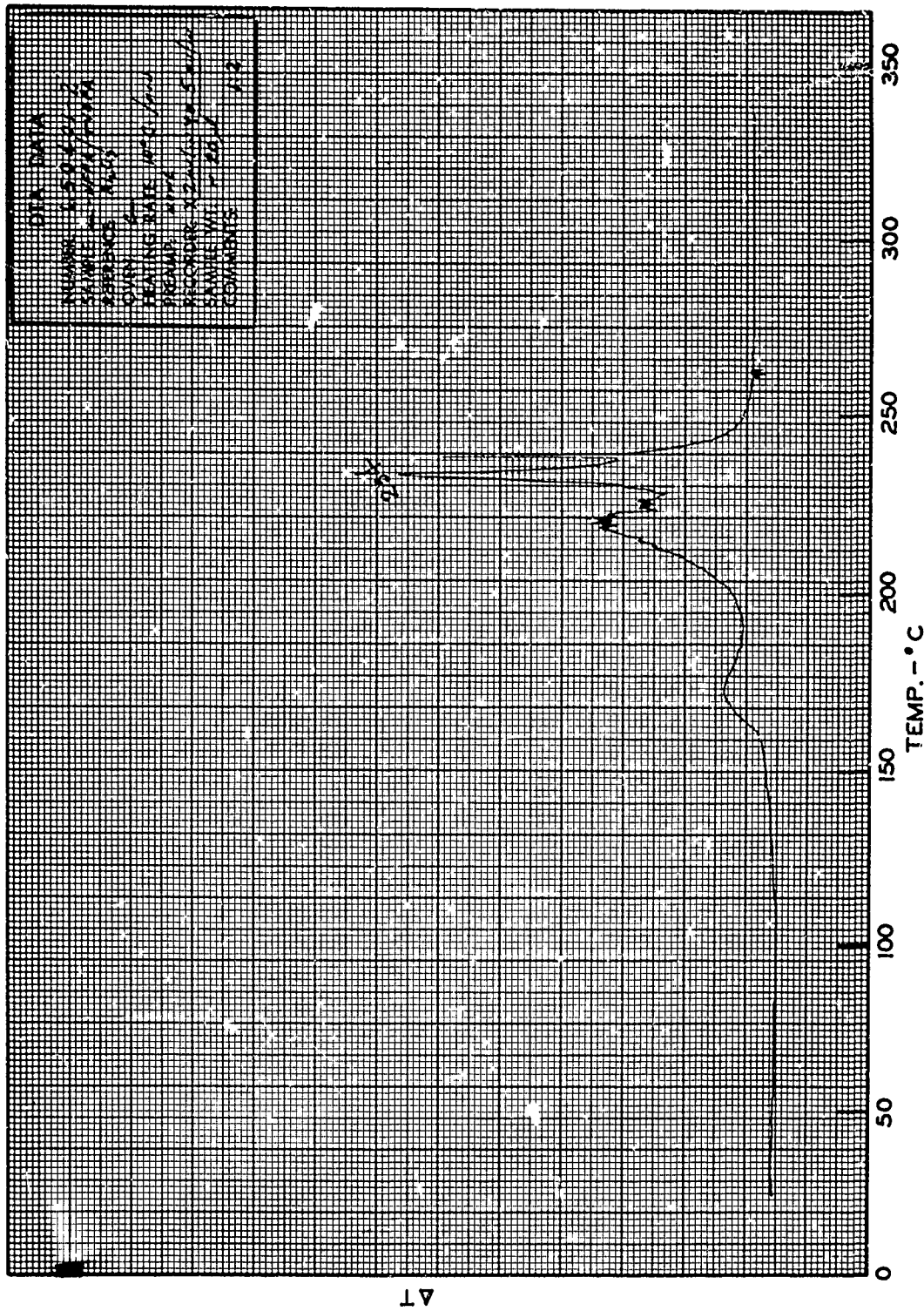
DIA DATA
 NUMBER: 650330-5
 SAMPLE: TVOPA / BORIC ACID
 REFERENCE: ALLOY
 OVEN: C
 HEATING RATE: 10°C/min
 PREAMP: NONE
 RECORDER: X 2 mV/in
 SAMPLE WT: 20.5476g
 COMMENTS:

TVOPA/TBB

THERMOGRAM NO. 38

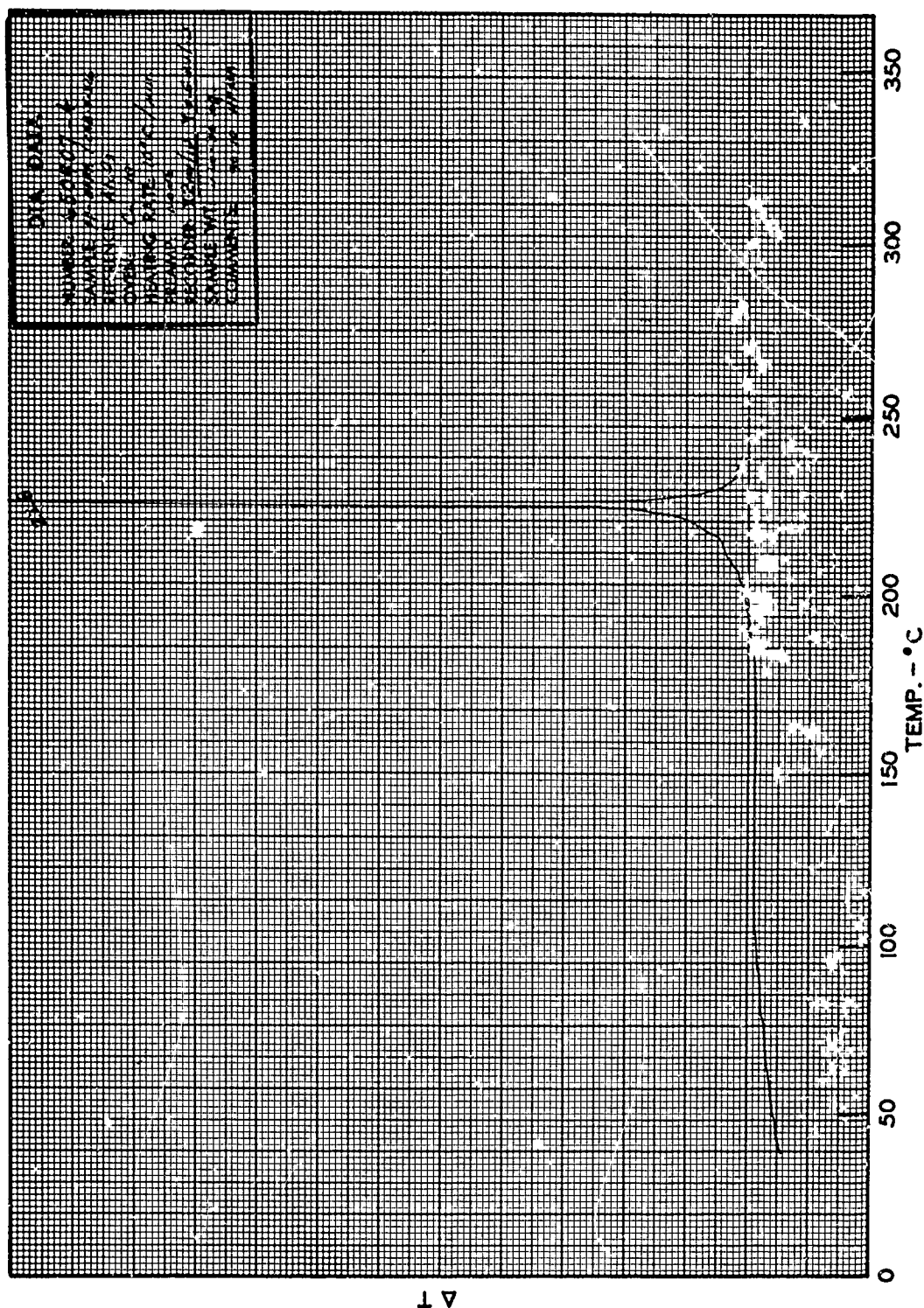


m-NFPA / TVOPA



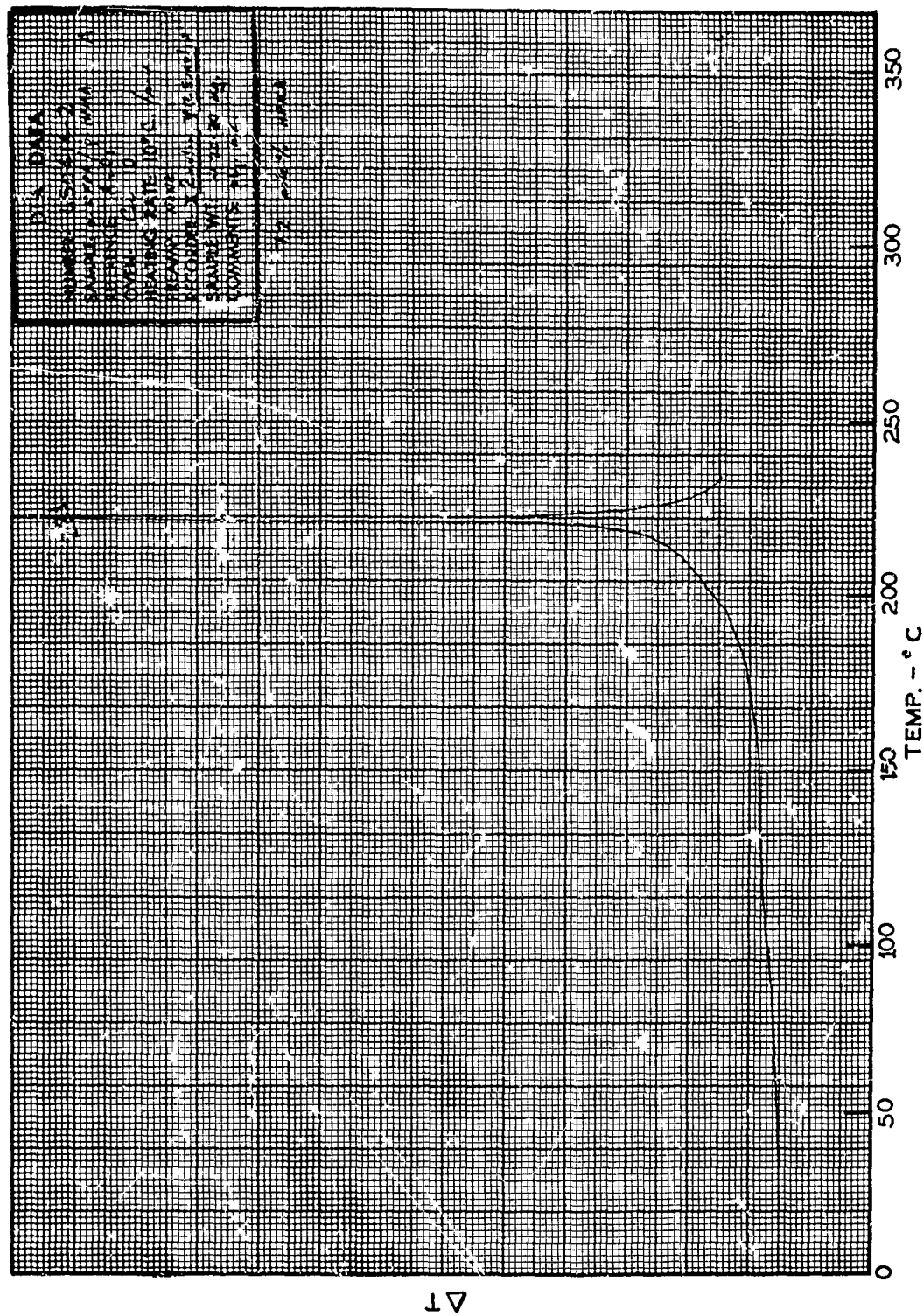
THERMOGRAM NO. 40

pp-NFPA / CAB·O·SIL

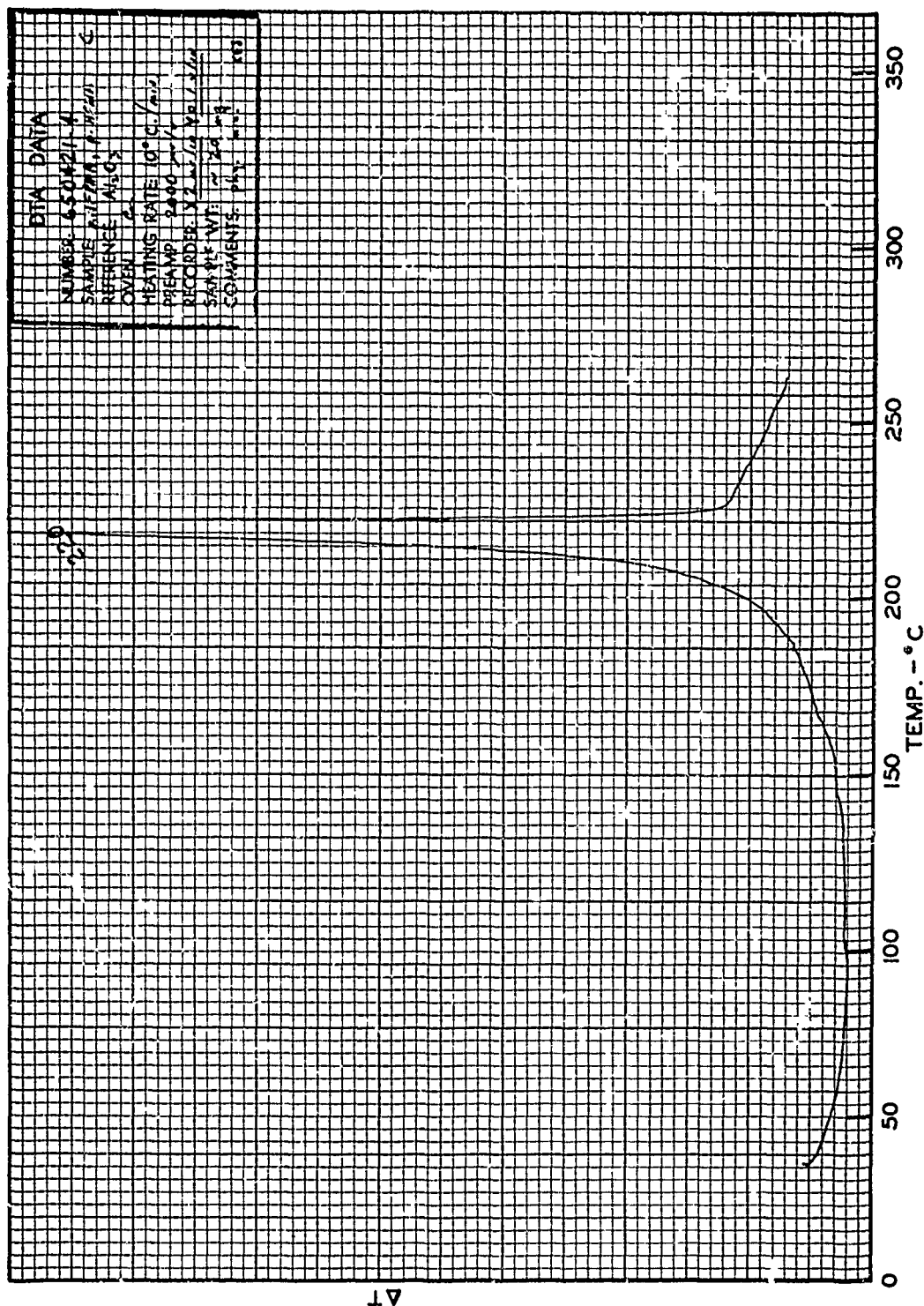


THERMOGRAM NO. 41

p-NFPA / p-HPMA

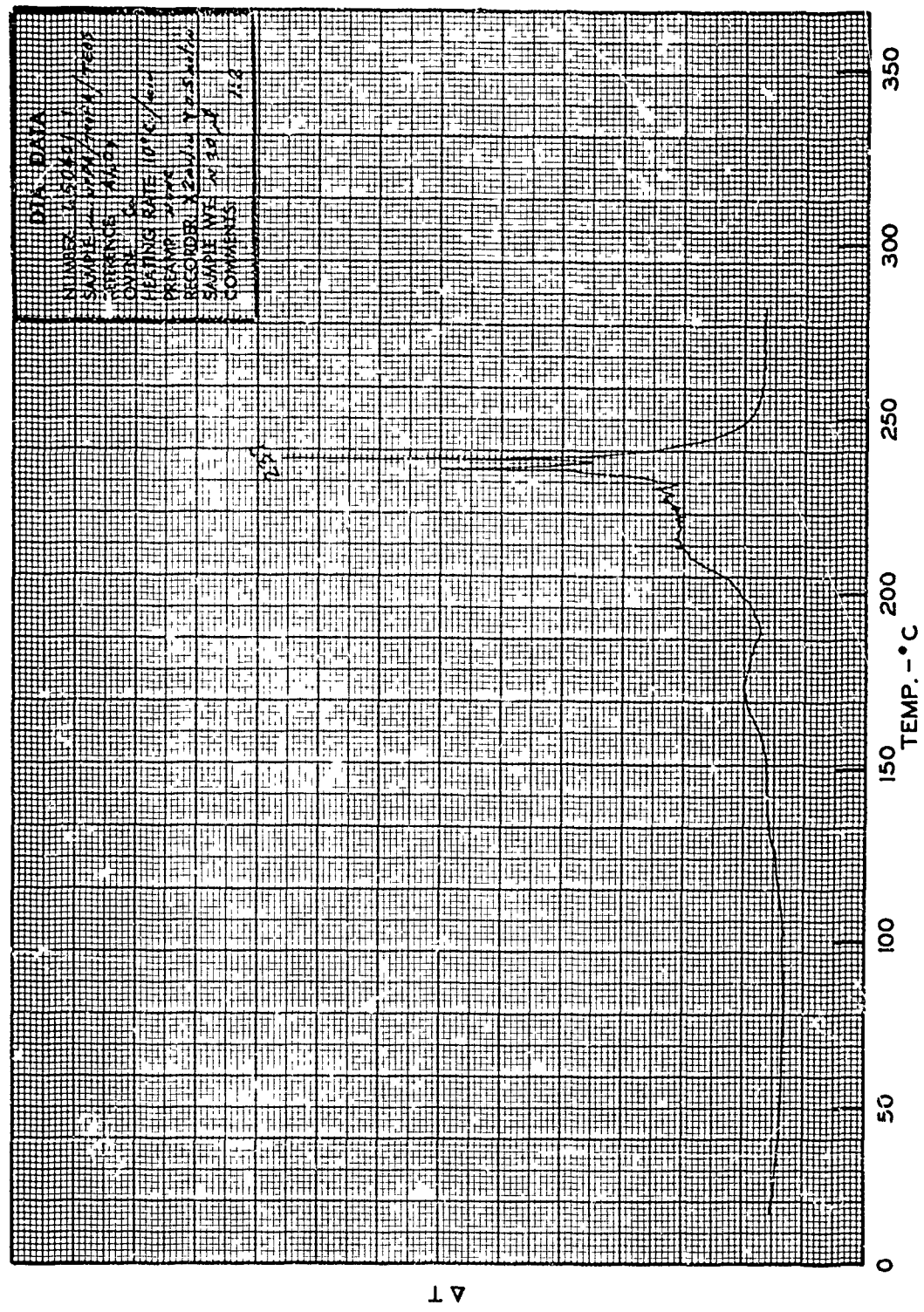


p - NFPMA / p - HPMA



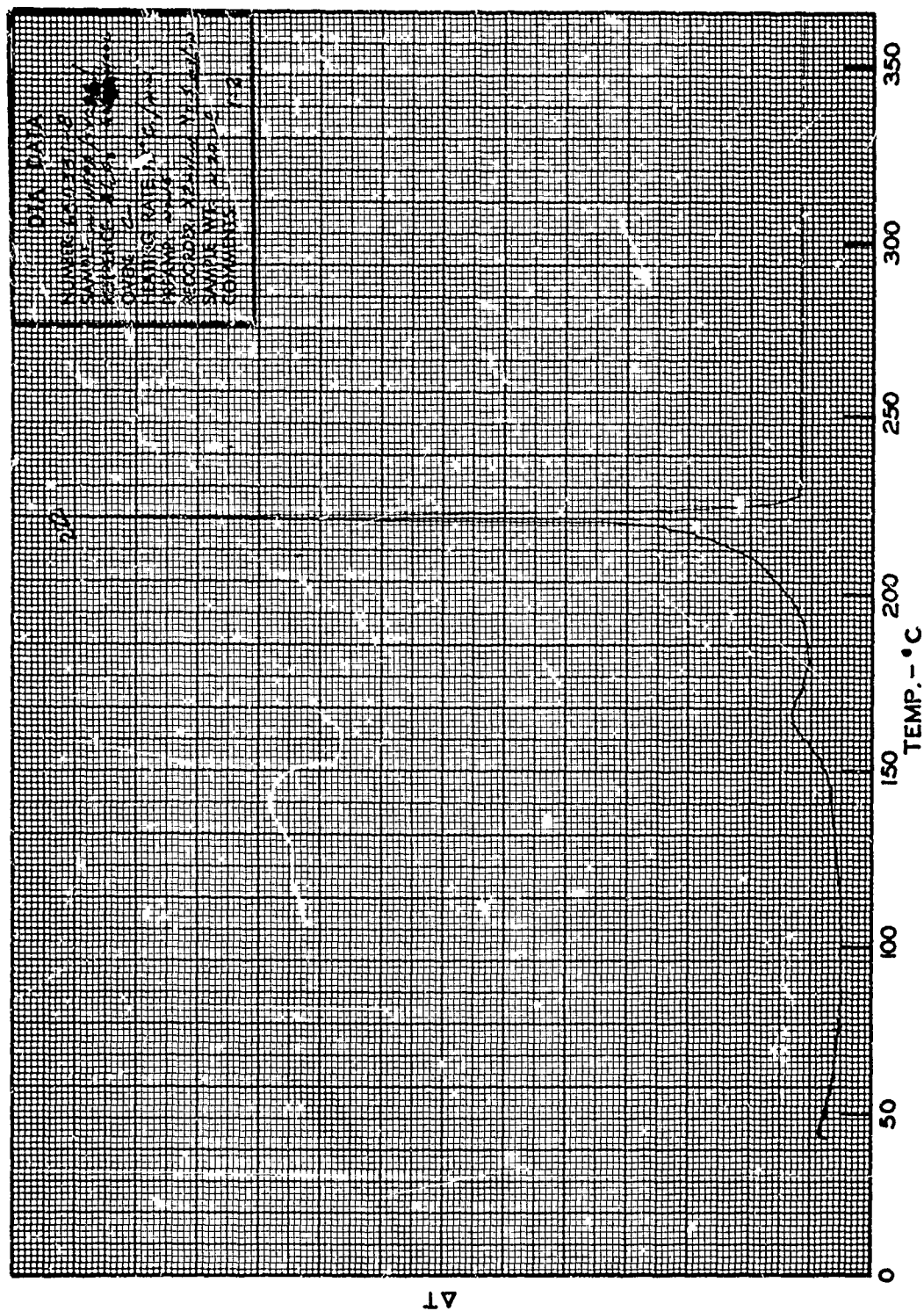
m - NFPA / TVOPA / TEOS

THERMOGRAM NO. 43



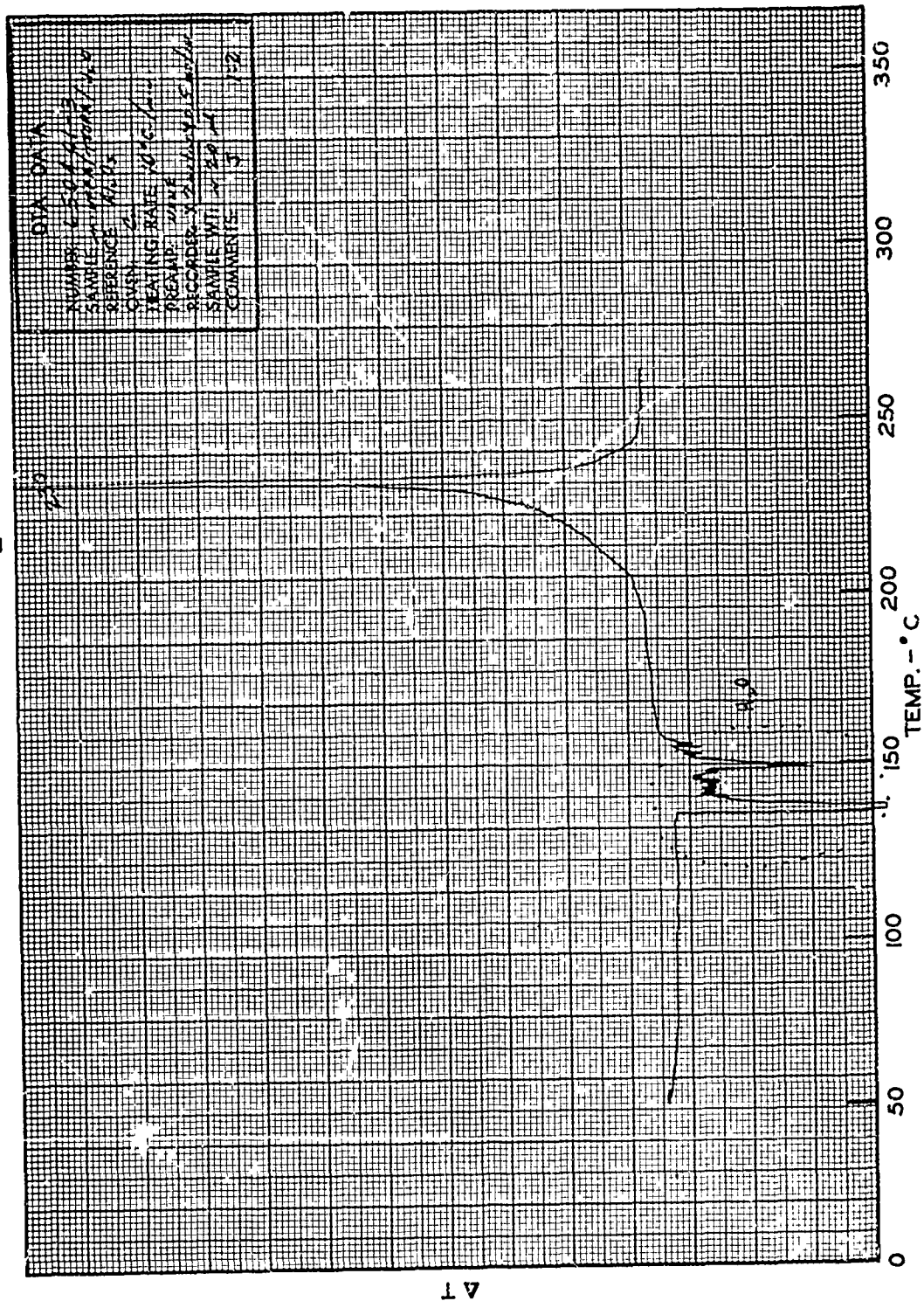
THERMOGRAM NO. 44

m - NFPA / TVO?? / GLASS WCOL



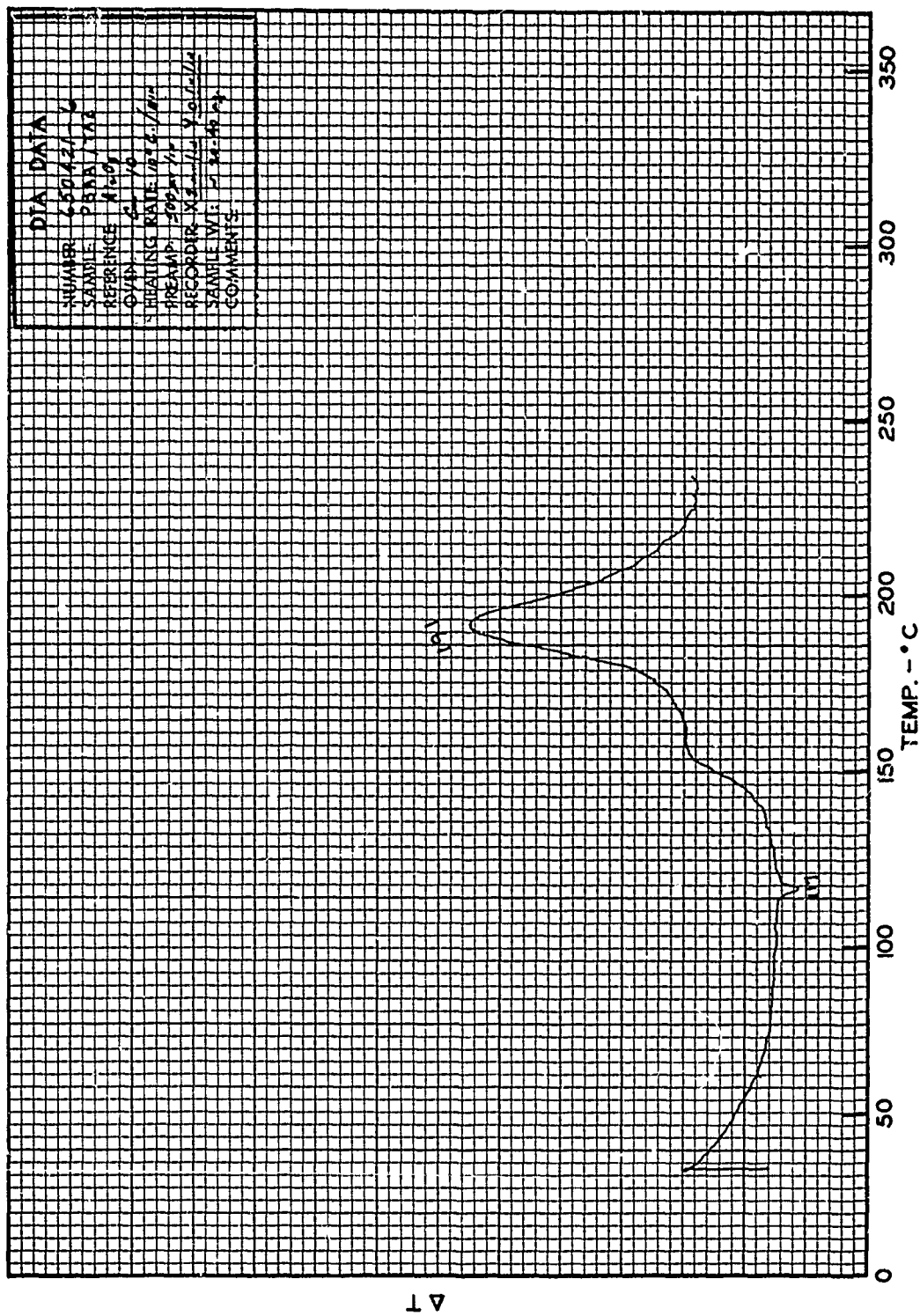
THERMOGRAM NO. 45

m - NFPA / TVOPA / H₂O



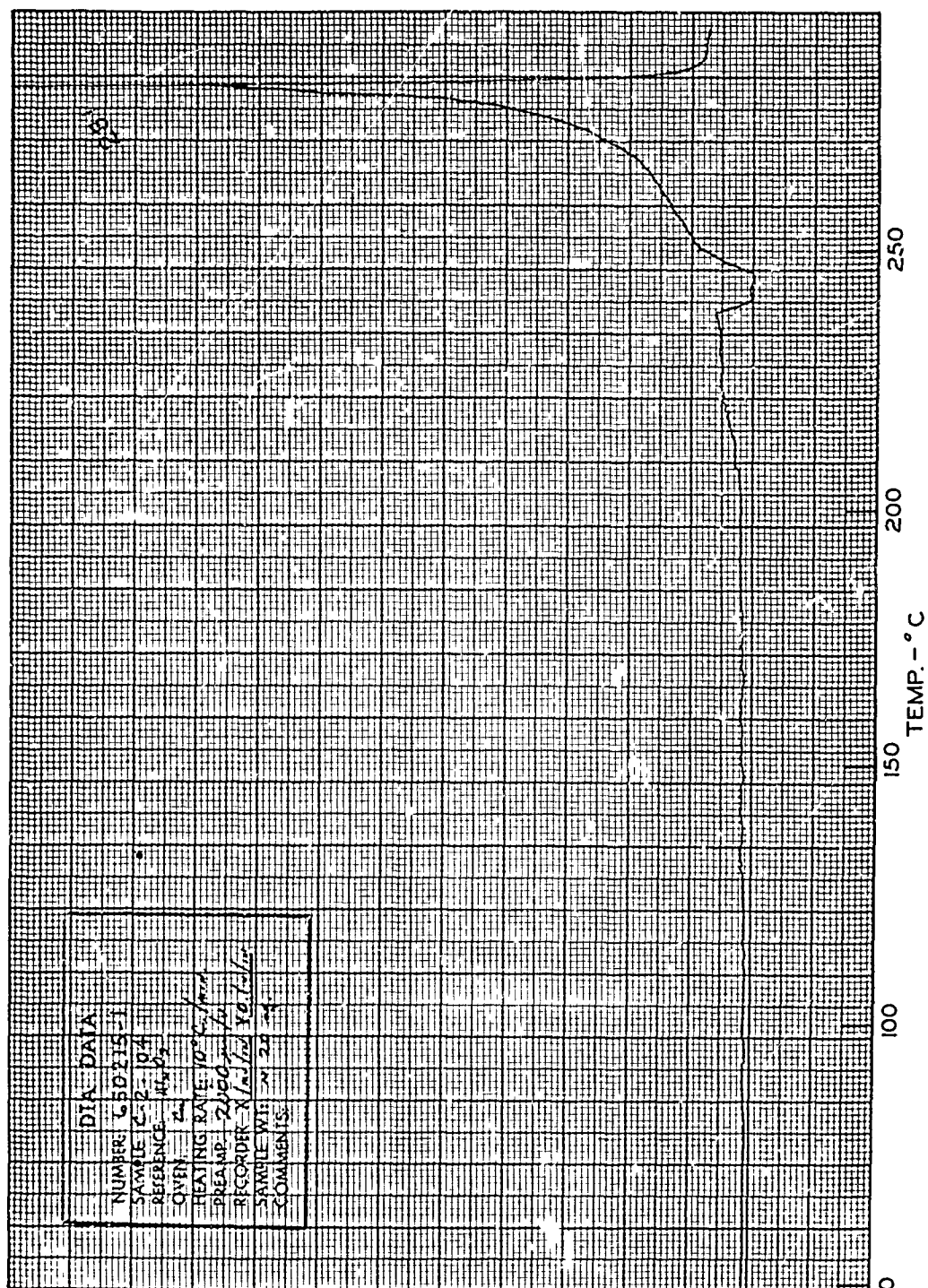
PBAA / TAZ

THERMOGRAM NO. 46



THERMOGRAM NO. 47

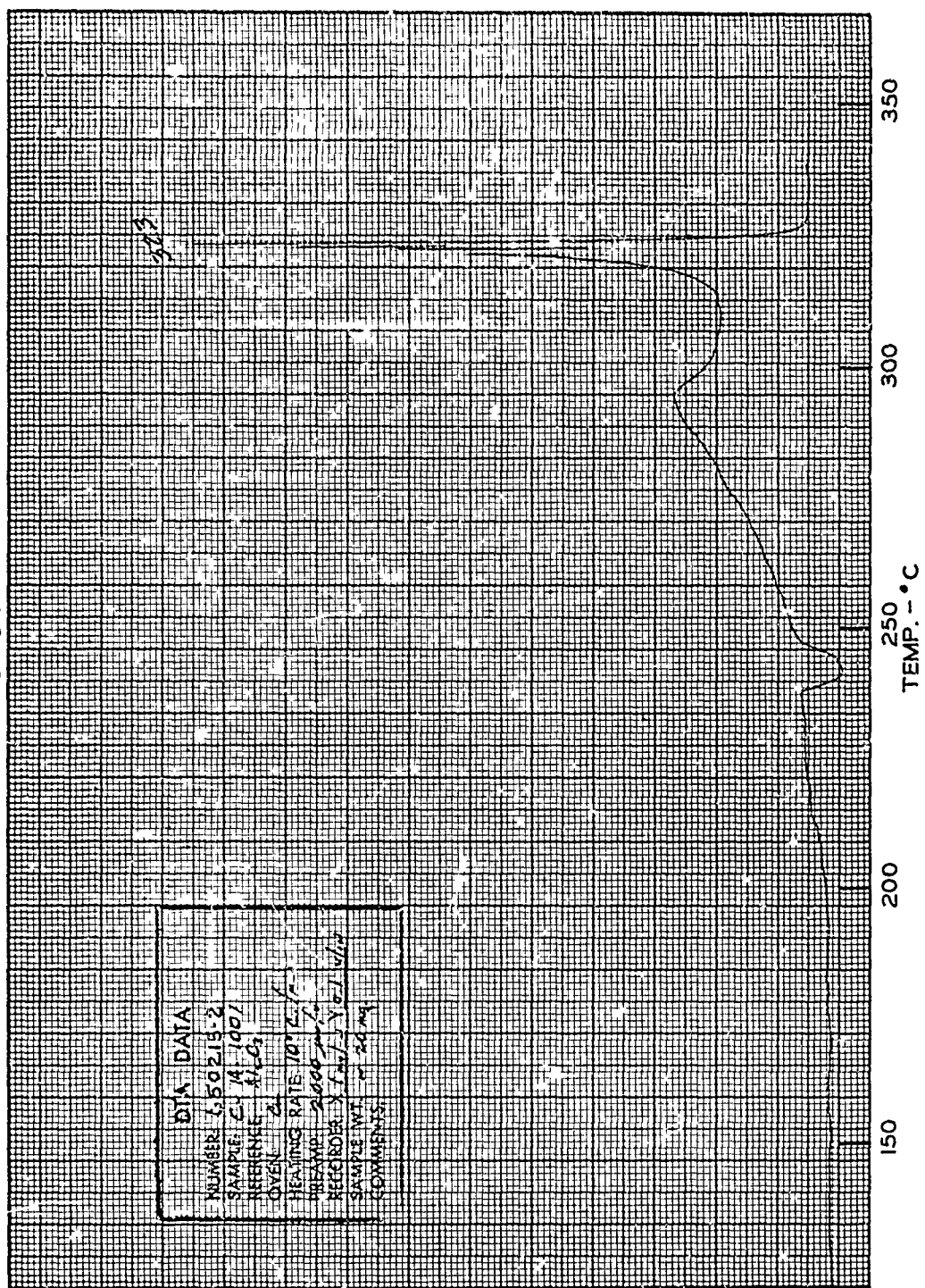
C-2



41

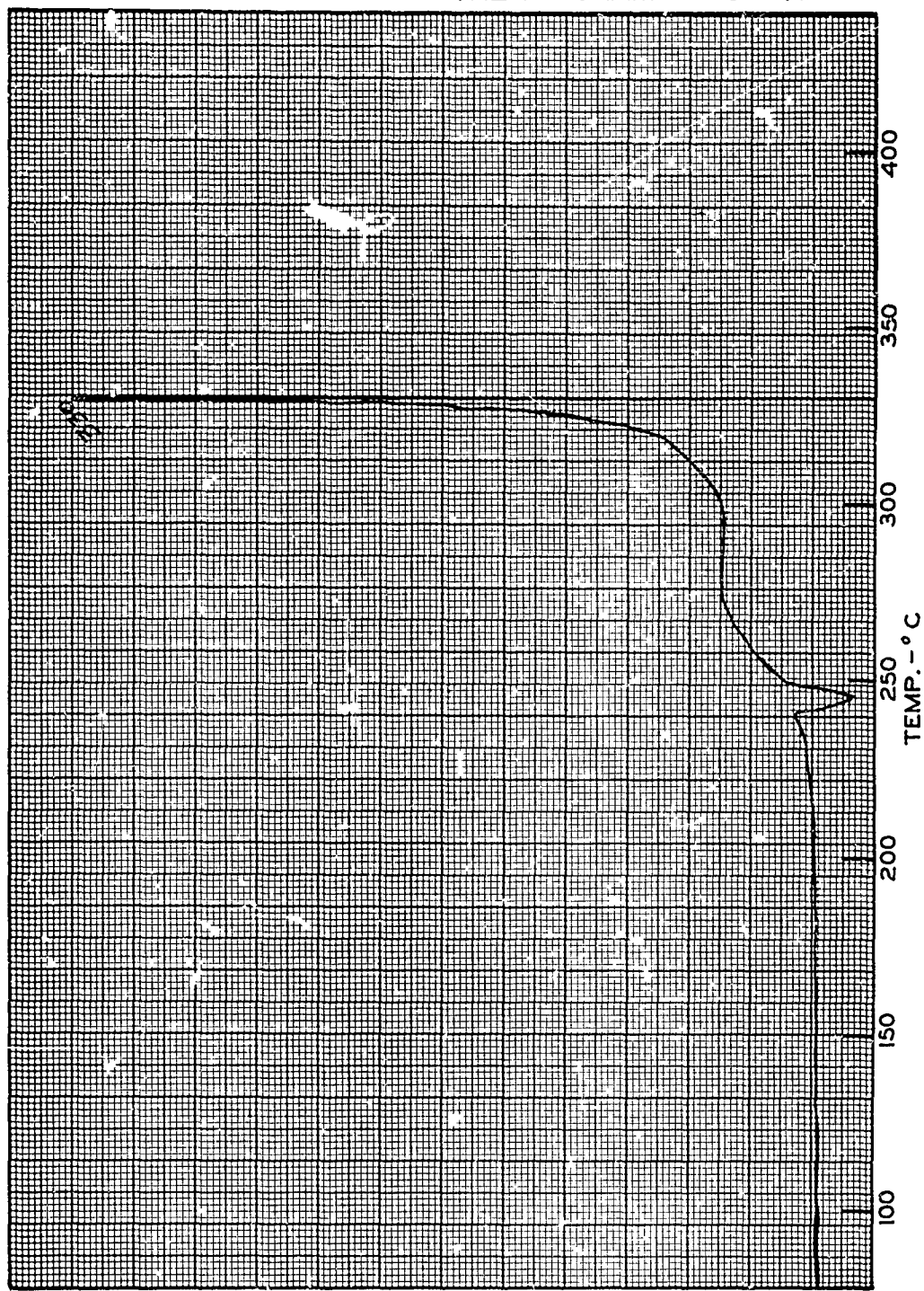
THERMOGRAM NO. 48

C-14



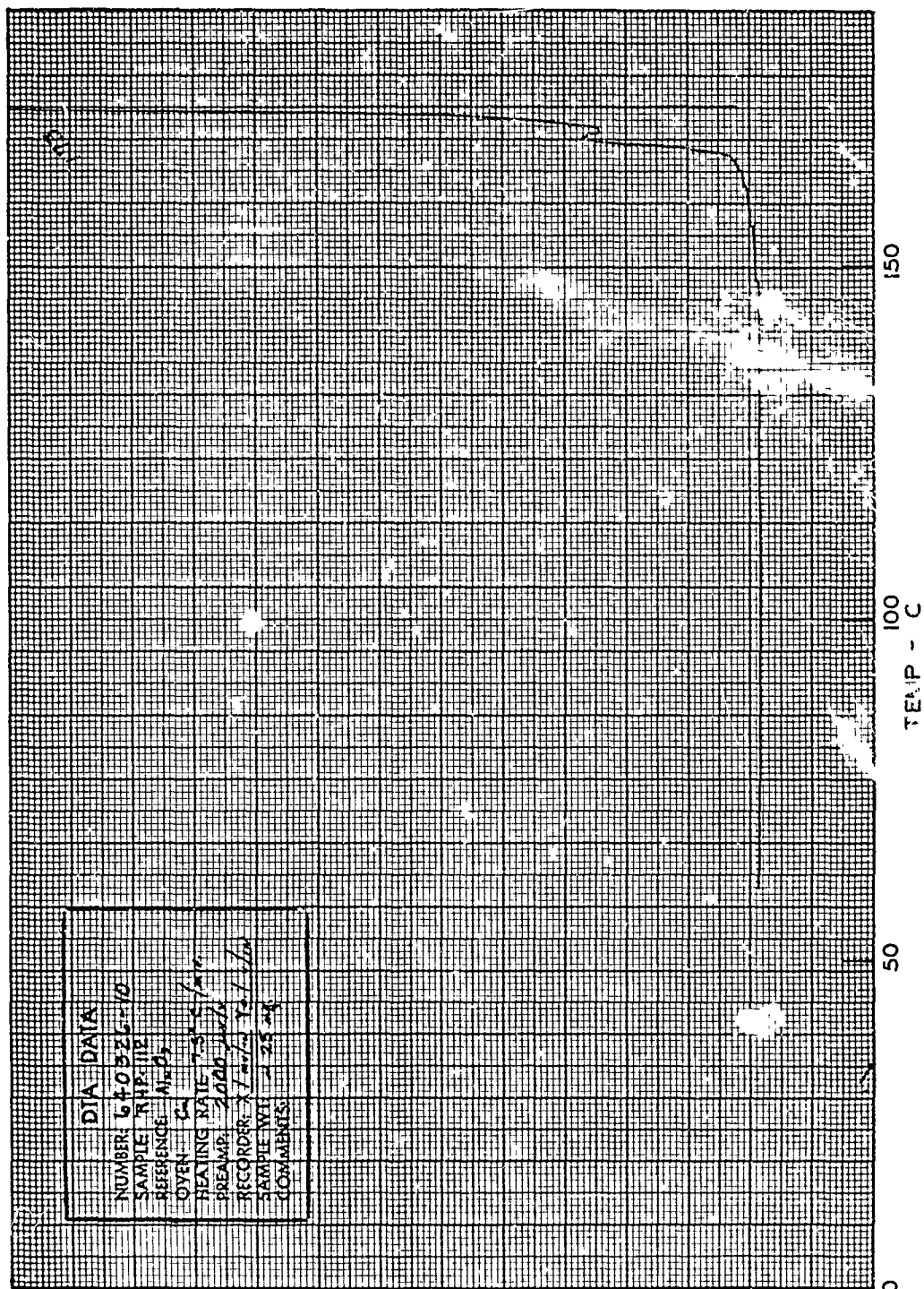
THERMOGRAM NO. 49

PBAA



THERMOGRAM NO. 50

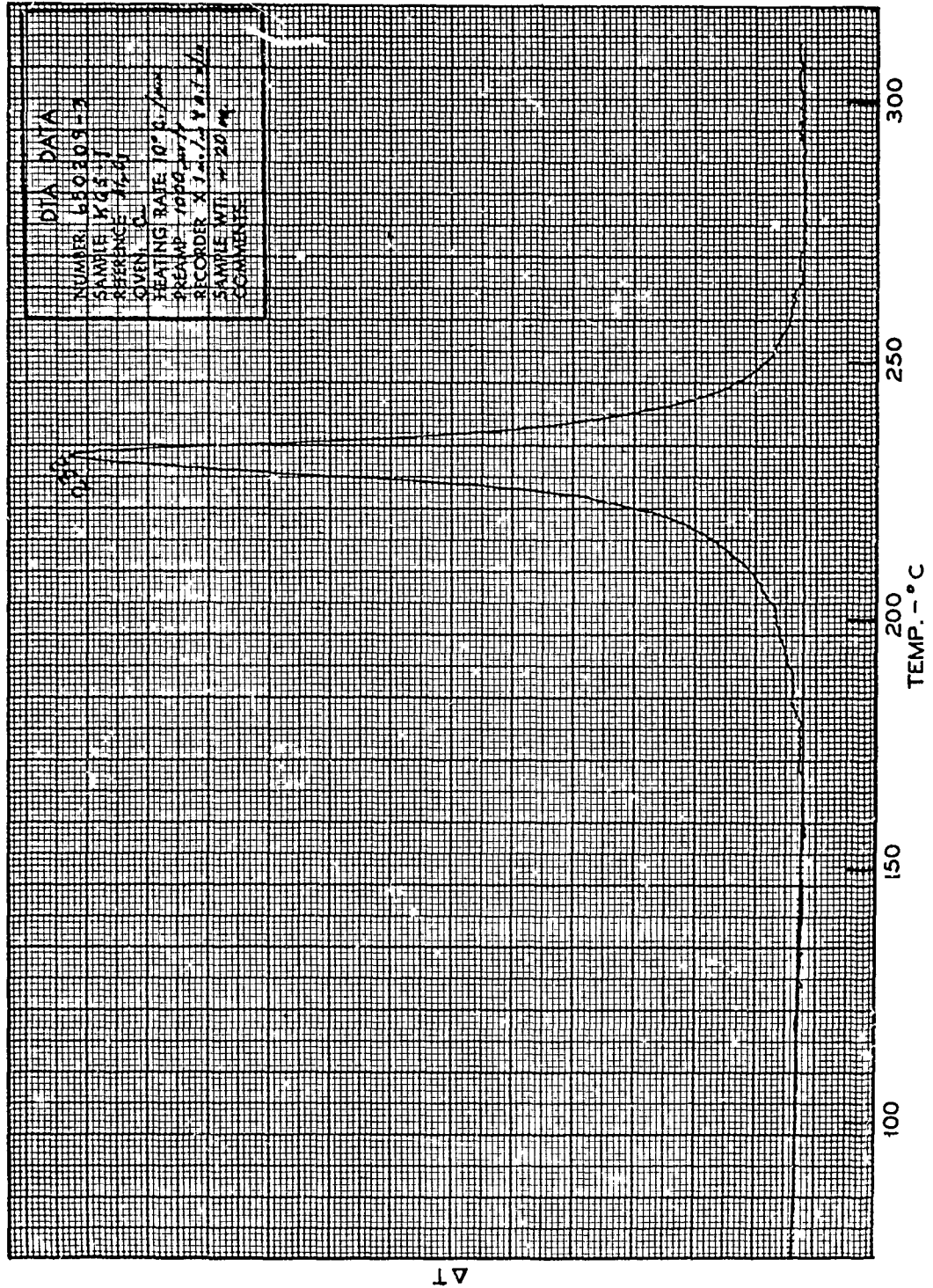
RHP-112



ΔT

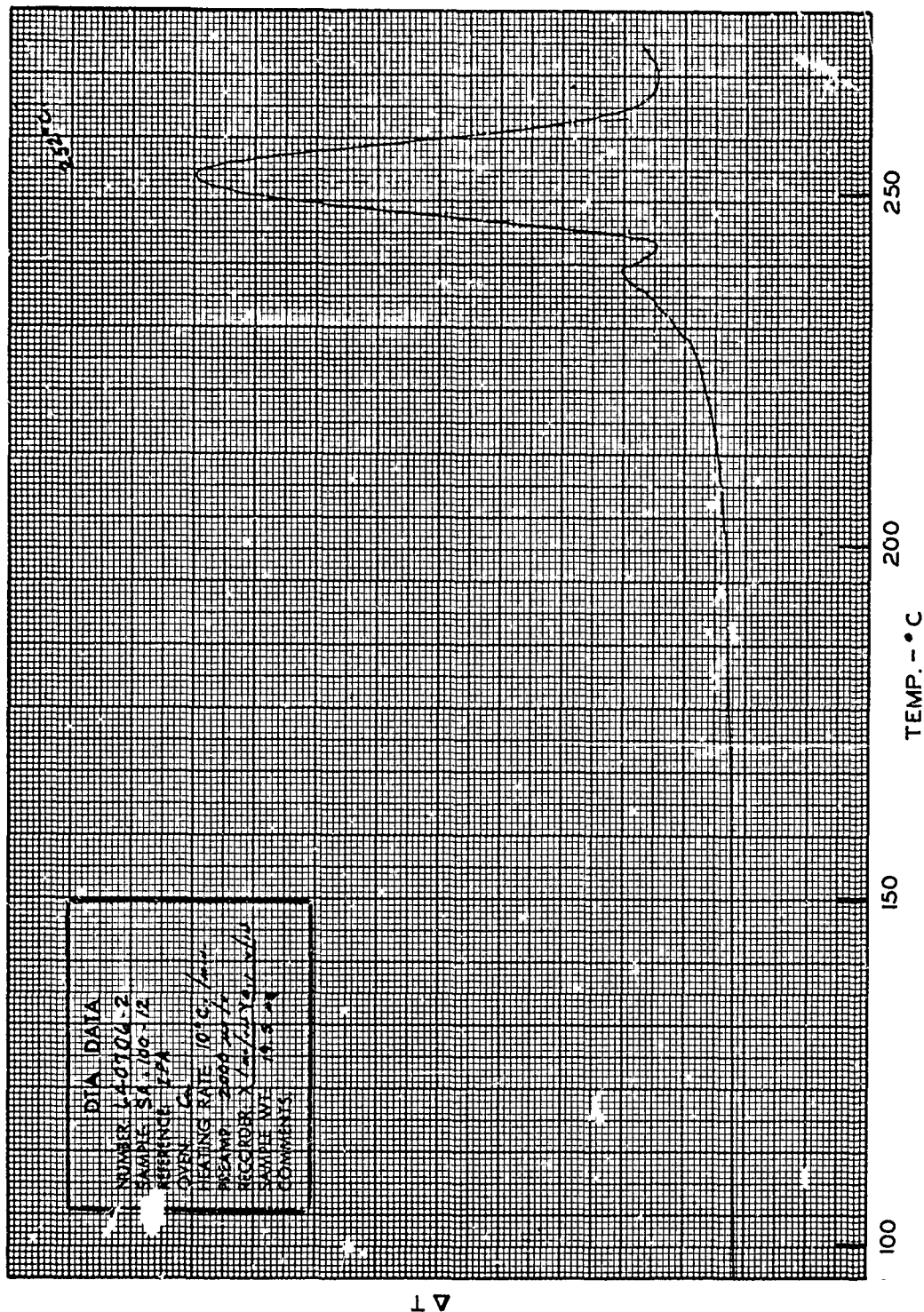
THERMOGRAM NO. 51

KGS-I



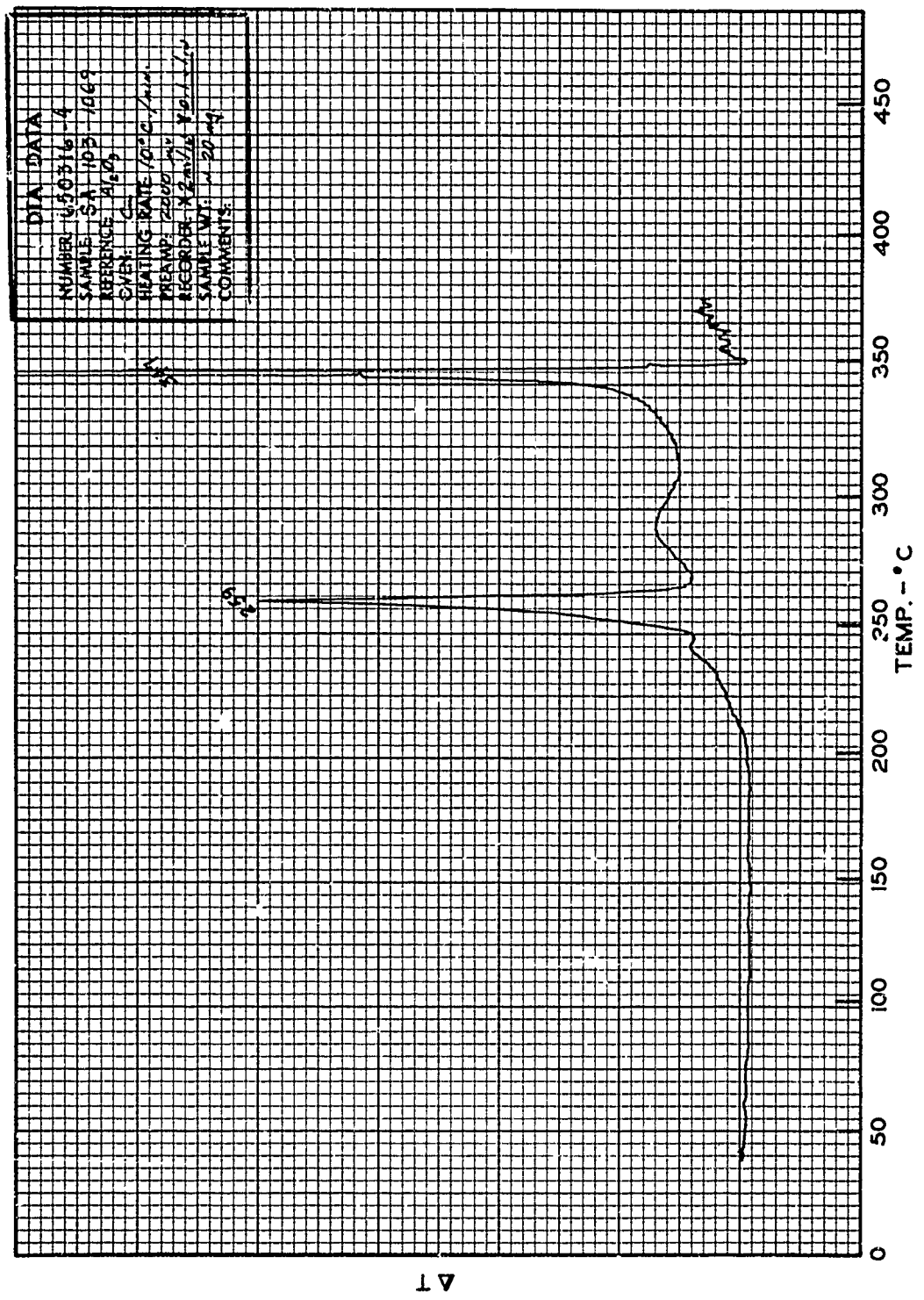
THERMOGRAM NO. 52

SA - 100



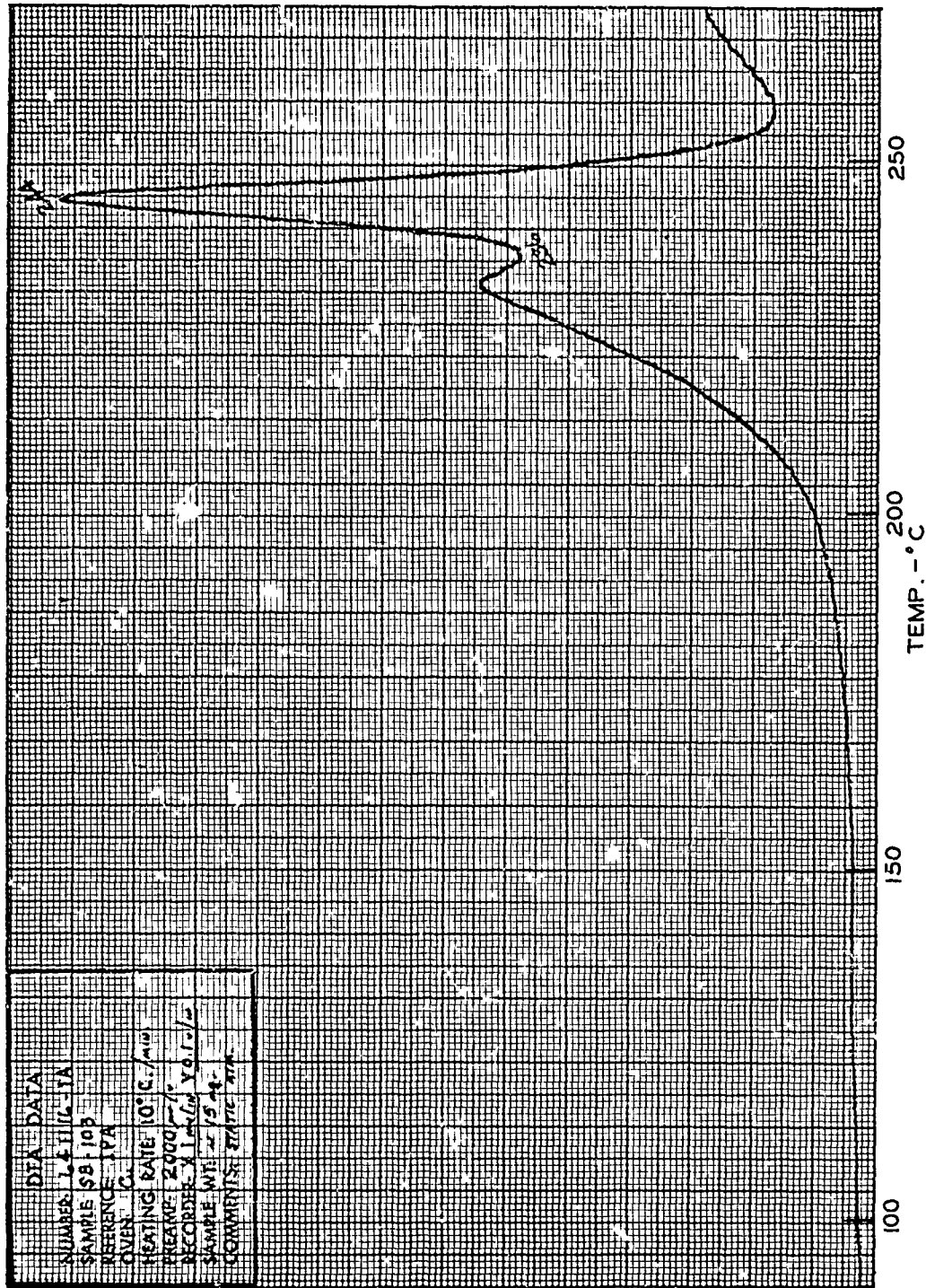
THERMOGRAM NO. 53

SA - 103



THERMOGRAM NO. 54

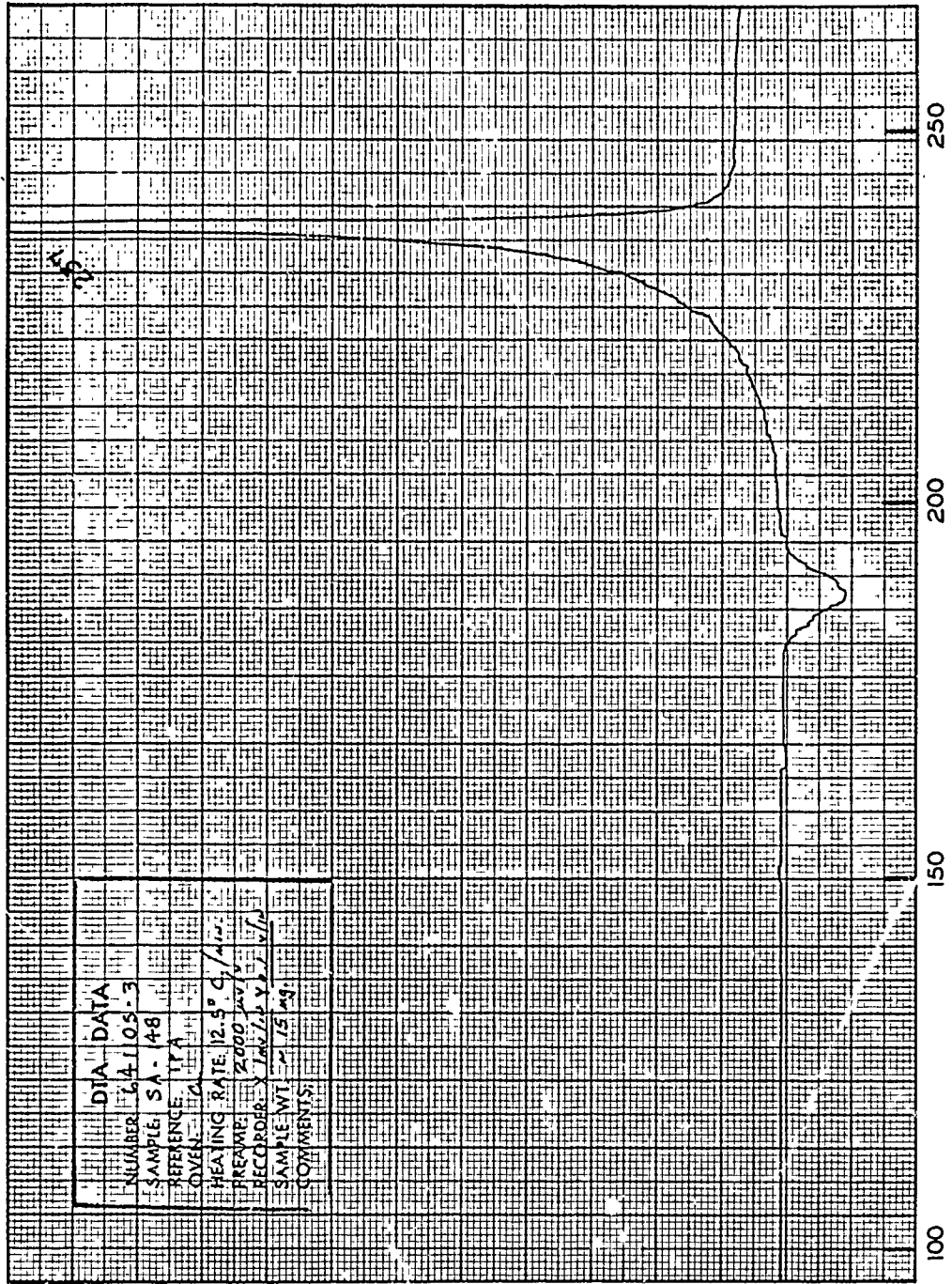
SB-103



ΔT

THERMOGRAM NO. 55

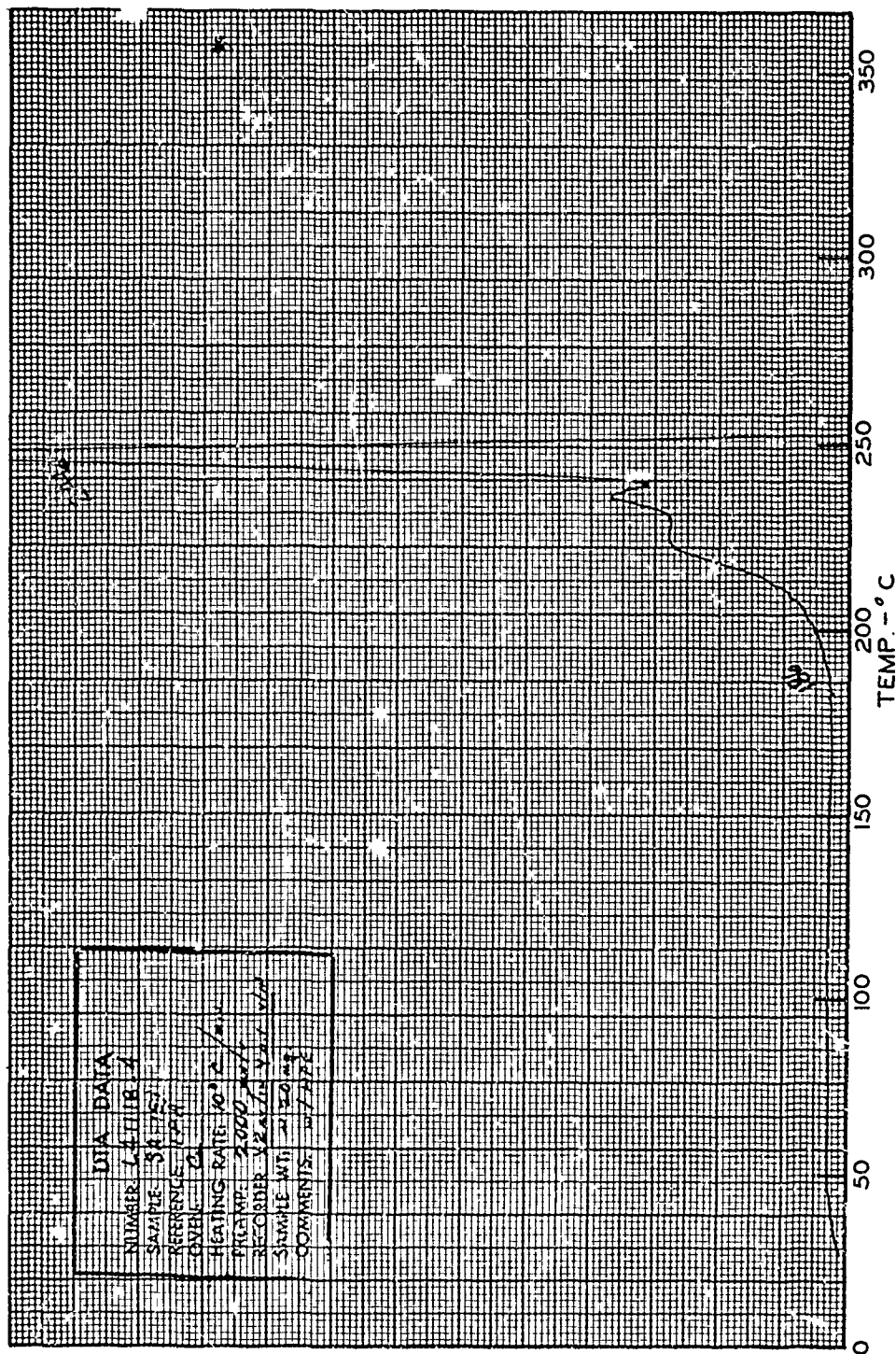
SA-148



ΔT

THERMOGRAM NO. 56

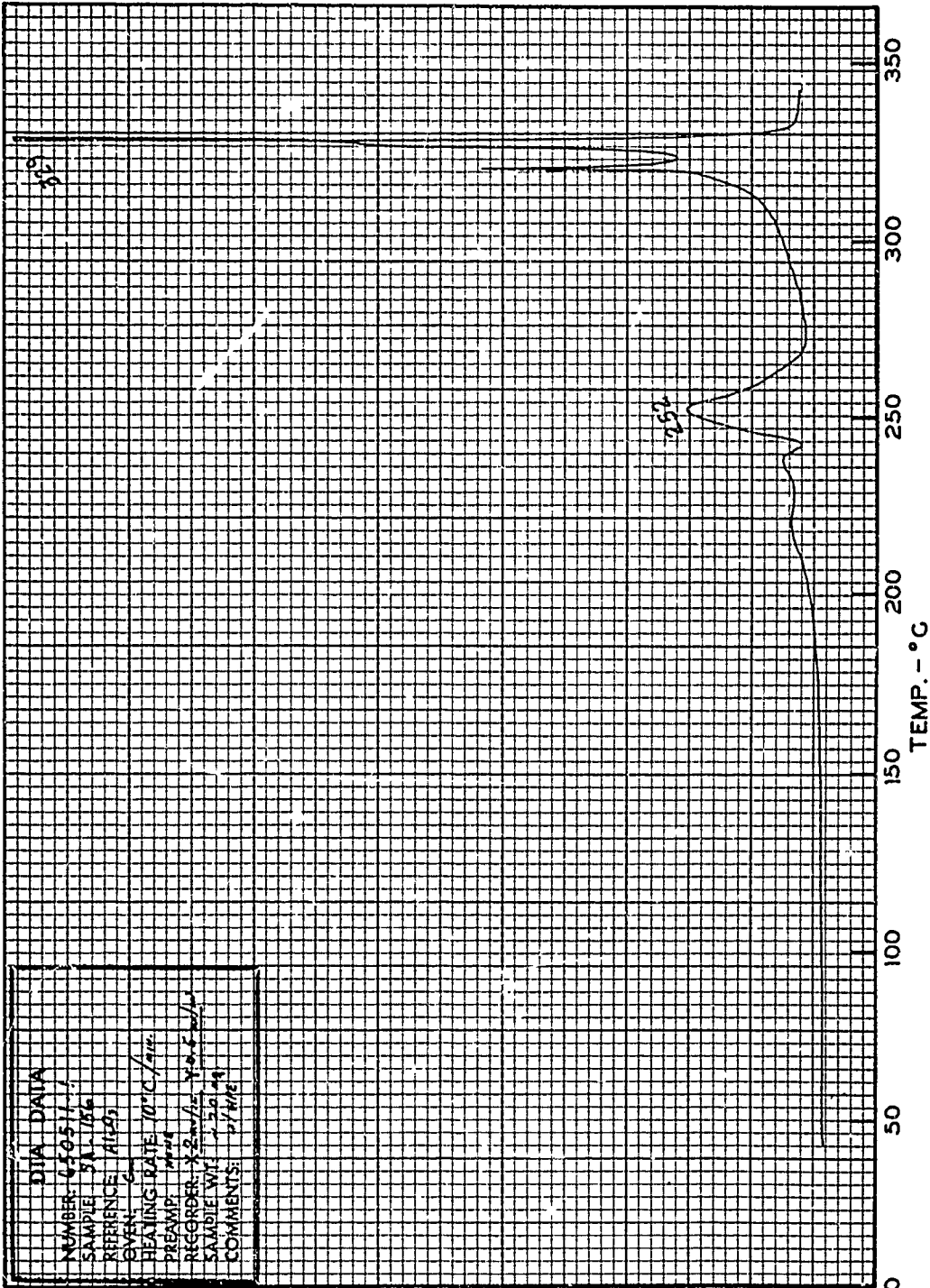
SA - 151



ΔT

THERMOGRAM NO. 57

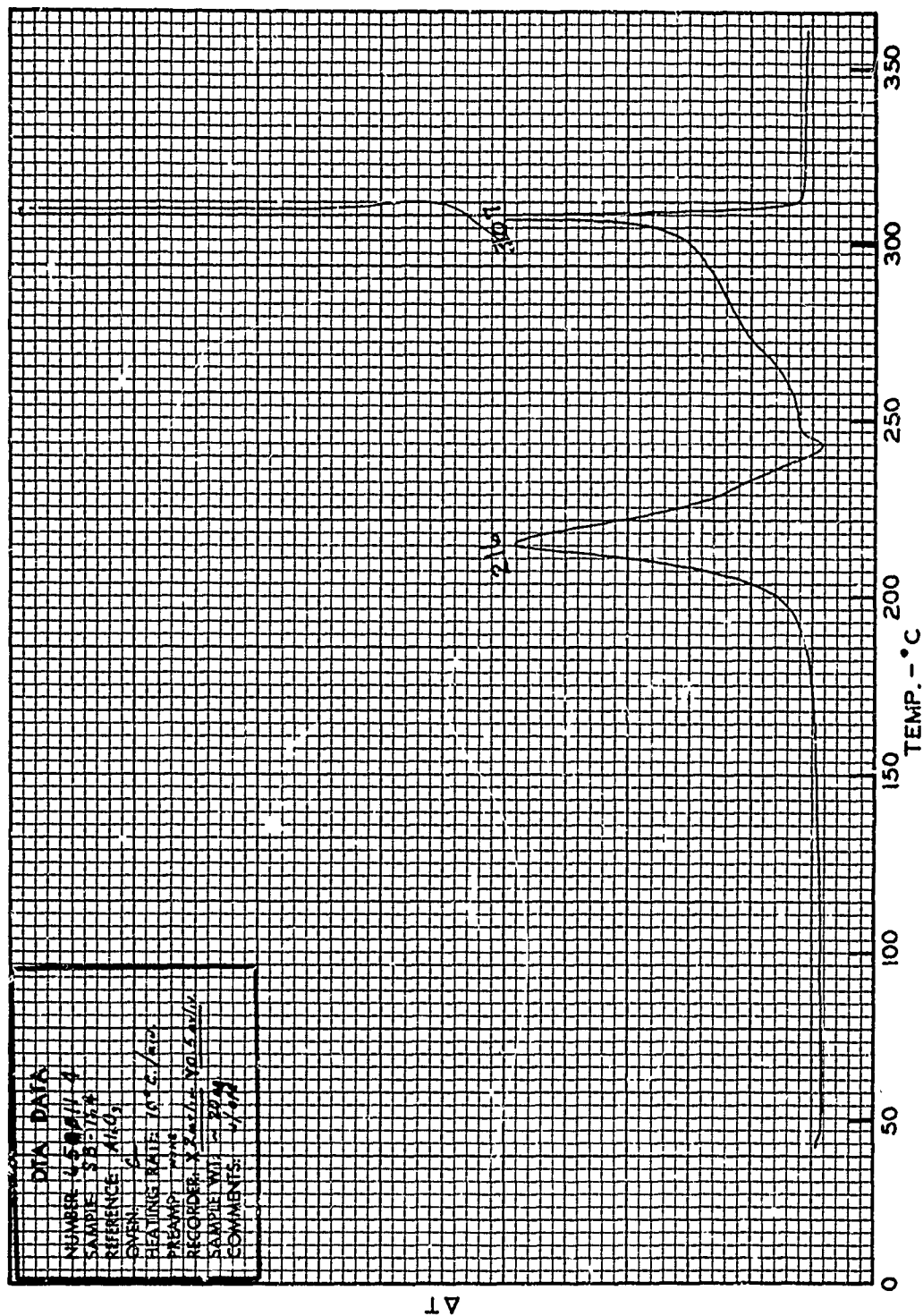
SA - 156



DATA DATA
NUMBER: 650511-1
SAMPLE: SA-156
REFERENCE: A1603
GIVEN: 6m
HEATING RATE: 10°C/min
PREAMP: none
REORDER: X 2.00/12 Y 0.50/12
SAMPLE WT: 2.5014g
COMMENTS: v/H/E

THERMOGRAM NO. 58

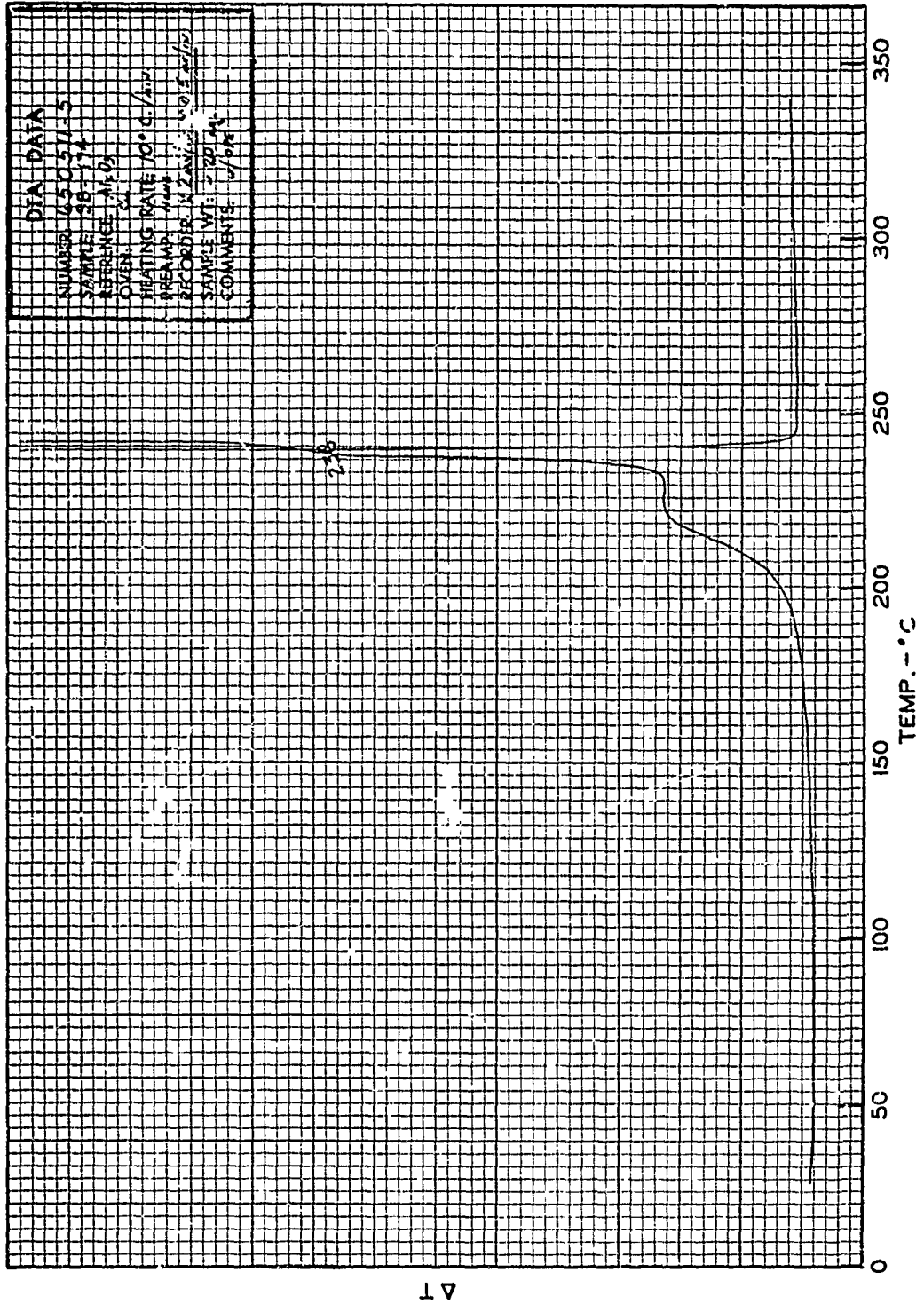
SB-164



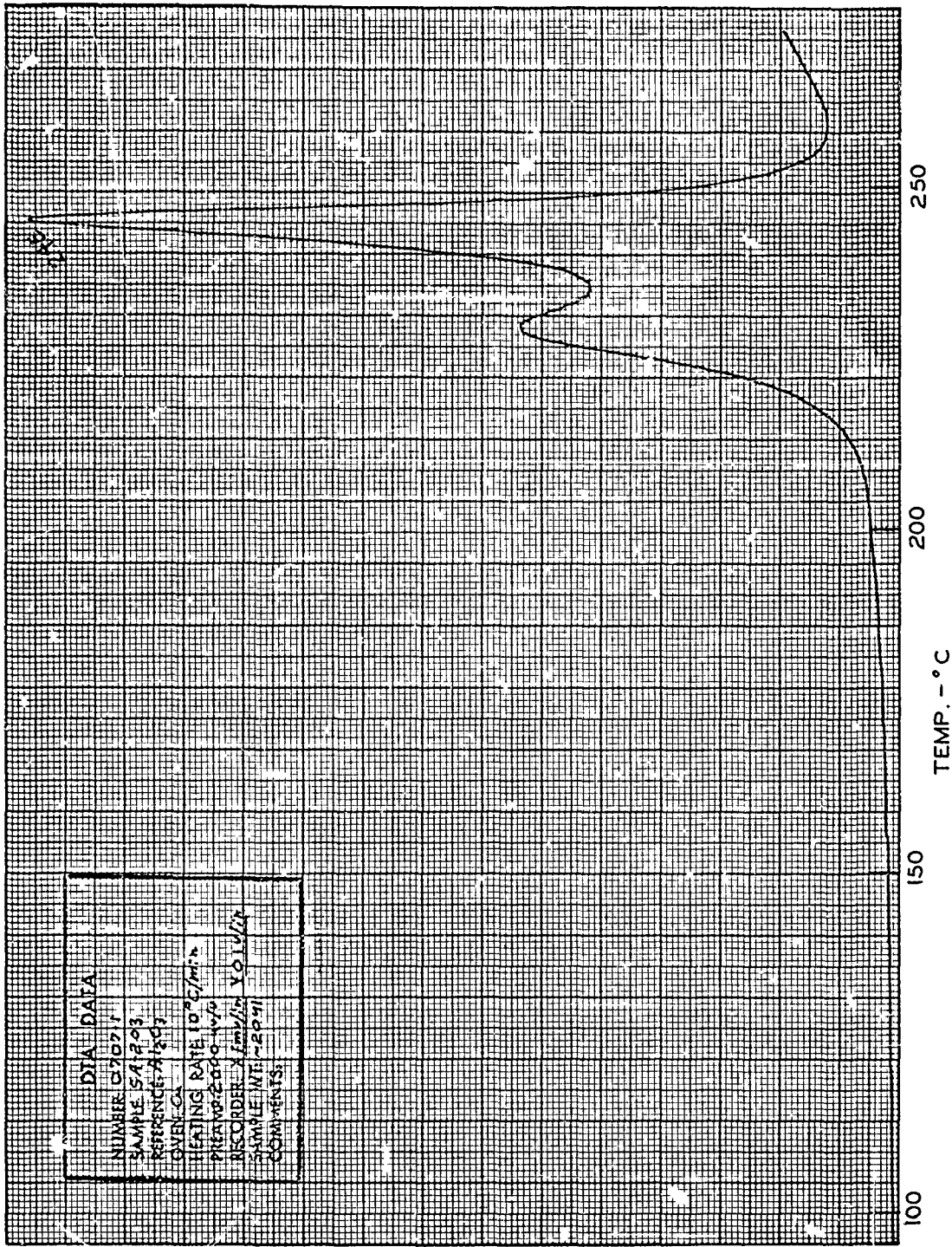
DATA DATA
 NUMBER 458411-1
 SAMPLE SB-164
 REFERENCE Al_2O_3
 OVEN 6
 HEATING RATE 10°C/min
 PREAMP none
 RECORDER XZ-2000 VOLTAGE
 SAMPLE WT 0.024
 COMMENTS 1/1/74

THERMOGRAM NO. 59

SB-174



SA-203



DATA	
NUMBER	07071
SAMPLE	SA-203
REFERENCE	A103
OVER	CA
HEATING RATE	10 °C/min
PREAMP	2000 x
RECORD	X 1mV/in
SAMPLE INT.	20m
COMMENTS	

ΔT

CONFIDENTIAL

APPENDIX B

Composition of Propellants

<u>RH-C-2</u>		<u>RH-C-14</u>		<u>PBAA</u>	
ZL-434-MAPO-ERLA	10.0	ZL-434-MAPO-ERLA	10.0	PBAA	25.0
Diocetyl Adipate	5.0	Diocetyl Adipate	5.0	AP	67.0
Iron Linoleate	0.1	Iron Linoleate	0.1	Al	8.0
AP	68.9	AP	67.9		
Al	16.0	Al	16.0		
		Ferrocene	1.0		
<u>RH-P-112</u>		<u>KGS-1</u>		<u>RH-SA-100</u>	
NC	16.7	NFPA	13.0	NFPA	15.0
TEGDN	37.3	TVOPA	26.0	TVOPA	15.0
AP	27.0	KCl	46.0	AP	55.0
Al	18.0	Al	15.0	Al	15.0
Resorcinol	1.0				
<u>RH-SA-103</u>		<u>RH-SB-103</u>		<u>RH-SA-148</u>	
NFPA	13.0	NFPA (pp)	13.0	NFPA	15.0
TVOPA	26.0	TVOPA	26.0	AA^	15.0
AP	46.0	AP	46.0	AP	55.0
Al	15.0	Al	15.0	Al	15.0
<u>RH-SA-151</u>		<u>RH-SA-156</u>		<u>RH-SB-164</u>	
NFPA	15.0	NFPA	13.0	NFPA(pp)	13.0
HPE	15.0	HPE	26.0	OPE	26.0
AP	55.0	X-970	+2.5	AP	46.0
Al	15.0	AP	46.0	Al	15.0
		Al	15.0		

CONFIDENTIAL

CONFIDENTIAL

APPENDIX B (continued)

<u>RH-SB-174</u>		<u>RH-SA-203</u>	
NFPA	12.5	TNFPA	13.0
OPE	37.5	TVOPA	26.0
AP	40.3	AP	46.0
Al	9.7	Al	15.0

CONFIDENTIAL